I. Introduction

Organic photovoltaics (OPVs) have attracted significant attention owing to their low-cost fabrication, low weight, and mechanical flexibility [1-3]. Generally, OPVs have a sandwich structure with an organic light-absorbing layer between the anode and cathode. In this multi-layer structure, interface engineering between the organic semiconductor and metal electrodes plays an important role in the device performance [4-6]. To attain high device performance, the basic requirement of the anode is a high work function. To increase the work function, a functional interlayer is inserted between the anode and p-type organic semiconductor. Additionally, an inverted structure of the OPVs, where the top electrode is used as an anode, is known to have a long device lifetime [7]. However, Al and Ag, which are commonly used as the top electrode materials, have low work functions that do not match the highest occupied molecular orbital (HOMO) level of a p-type organic semiconductor. Therefore, a functional interlayer is inserted between the light-absorbing layer and anode. OPVs with a dual-anode buffer layer have been reported to exhibit a superior performance than those with a single-anode buffer layer. Herein, the device performance of inverted OPVs with a poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C61-butyric acid methyl ester light-absorbing layer and dual-anode buffer layer of MoO3 and 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HAT-CN) is investigated. The power conversion efficiency (PCE) of the OPV with the HAT-CN/MoO3/Al anode system is lower than that with the conventional MoO3/Al anode system. However, the PCE of the OPV with MoO3/HAT-CN/Al is slightly higher than that with MoO3/Al. The change in the device performance by varying the deposition sequence of HAT-CN and MoO3 is discussed based on the built-in potential.

II. Experimental details

The inverted OPVs were fabricated with an Al/anode buffer layer/P3HT:PCBM/polyethylenimine ethoxylated (PEIE)/indium tin oxide (ITO) structure. An ITO-patterned glass substrate was cleaned by ultrasonication in deionized water, detergent, acetone, and methanol. This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (http://creativecommons.org/licenses/by-nc/3.0) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.
bath. It was then dried with N₂ gas flow and treated with ultraviolet ozone at 100 °C for 15 min. At the cathode buffer layer, PEIE (Sigma-Aldrich) was deposited by spin coating onto ITO at a spin rate of 5000 rpm for 60 s [13]. Subsequently, the sample was annealed at 100 °C for 10 min. P3HT (Mw: > 45,000, regioregularity: > 93 %) and PCBM (purity: > 99.5 %) were purchased from Luminescence Technology. P3HT and PCBM were dissolved in chlorobenzene (purity: > 99.9 %, Sigma-Aldrich) at a concentration of 80 mg mL⁻¹ (1:1 wt %) and stirred overnight before use. The P3HT:PCBM light-absorbing layer was deposited by spin coating onto PEIE/ITO from the mixed solution at a spin rate of 2000 rpm for 60 s. Then, the film was annealed at 150 °C for 15 min. All solution processes were accomplished at ambient conditions, and the annealing was performed using a hot plate. The sample was thereafter transferred into a vacuum chamber. MoO₃ (purity: > 99.97 %) was purchased from Sigma-Aldrich and HAT-CN (purity: > 99.9 %) from EM INDEX. MoO₃ (15 nm) and HAT-CN (5 nm) were deposited via thermal evaporation at a deposition rate of 0.01 nm s⁻¹. Finally, the 100 nm-thick Al layer was deposited via thermal evaporation with deposition rates of 0.01 nm s⁻¹ for the initial 10 nm thickness and 0.05 – 0.1 nm s⁻¹ for a thickness of 90 nm. The hole-only devices were fabricated with the Al/anode buffer layer/P3HT/poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS)/ITO structure. PEDOT:PSS (Clevios™ P VP AI 4083) was purchased from Heraeus. The PEDOT:PSS layer was deposited onto ITO by spin coating at a rate of 500 rpm for the initial 5 s, followed by 3000 rpm for the next 30 s, and then annealed at 150 °C for 10 min. Subsequently, the P3HT layer was deposited onto PEDOT:PSS/ITO by spin coating from a chlorobenzene solution at a concentration of 40 mg mL⁻¹, and then annealed at 150 °C for 15 min. The anode buffer layer and Al were deposited in the same manner as the OPVs. The device area of the OPVs and hole-only devices was 0.04 cm².

Current density-voltage (J-V) characteristics were measured using a Keithley 2400 source measure unit. The photovoltaic parameters were recorded under Air Mass 1.5G 1 sun illumination generated by a solar simulator (Model 10500, Abet Technologies). Capacitance-voltage (C-V) measurements were performed using a Solartron SI 1260 impedance/gain-phase analyzer. All measurements were performed at room temperature and ambient conditions. For the C-V measurements, a frequency of ~1000 kHz, in which the phase of impedance showed the closest value to 90°, was used. AC perturbation of 25 mV was employed.

III. Results and discussion

Figure 1 shows (a) the chemical structures of the organic materials (P3HT, PCBM, and HAT-CN), and (b) the energy-level alignment of the OPVs with the MoO₃ and HAT-CN dual-anode buffer layer used in this study. The energy levels are obtained from the charge transport levels measured by ultraviolet and inverse photoelectron spectroscopy [9,14,15] under the assumption of vacuum-level alignment. P3HT and PCBM were used as the donor and acceptor, respectively. Owing to the low work function of PEIE, the cathode interface was efficiently contacted. HAT-CN has a deep HOMO level and high work function, similar to MoO₃ [15,16]. However, the reported transport gap of HAT-CN is much larger than that of MoO₃.

Figure 2(a) shows the J-V characteristics of the inverted OPVs upon 1 sun illumination. The J-V curve indicates an average performance among the 32 devices. The inset shows the schematic of the
inverted OPV device structure. The photovoltaic parameters and OPV statistics are summarized in Table I. The OPVs with a single MoO3 anode buffer layer show a short-circuit current density ($J_{SC}$) of 10.60 ± 0.34 mA cm$^{-2}$, open-circuit voltage ($V_{OC}$) of 0.63 ± 0.004 V, and fill factor (FF) of 56.6 ± 2.12 %, which yields a PCE of 3.74 ± 0.20 %. However, when the HAT-CN/MoO3/Al anode system is used, all photovoltaic parameters are significantly reduced. The OPVs with HAT-CN/MoO3/Al show a $J_{SC}$ of 10.28 ± 0.34 mA cm$^{-2}$, $V_{OC}$ of 0.58 ± 0.008 V, FF of 53.1 ± 1.38 %, and PCE of 3.19 ± 0.12 %. However, when the MoO3/HAT-CN/Al anode system is employed, the PCE of the OPVs is only slightly increased. The OPVs with MoO3/HAT-CN/Al show a $J_{SC}$ of 11.40 ± 0.32 mA cm$^{-2}$, $V_{OC}$ of 0.63 ± 0.005 V, and FF of 55.6 ± 1.38 %, resulting in a PCE of 3.97 ± 0.12 %. Although the FF of the OPVs with MoO3/HAT-CN/Al decreases in comparison to that with a single MoO3 anode buffer layer, $V_{OC}$ does not change, and $J_{SC}$ increases. The reduced FF with the insertion of the additional HAT-CN layer can be attributed to an increase in the series resistance due to an increase in the total thickness. In contrast, the slightly improved $J_{SC}$ values of the OPVs with MoO3/HAT-CN/Al may be due to the enhancement of the light-absorbing ability via optical interference by the increased thickness [17].

Figure 2(b) shows a semi-log plot of the $J$-$V$ characteristics of the OPVs under dark conditions. The inset shows a linear plot of the $J$-$V$ characteristics. At 0.7 V, the OPV with MoO3/HAT-CN/Al records the highest $J_{SC}$ value, but similar to that for MoO3/Al. The OPV with HAT-CN/MoO3/Al shows the lowest $J_{SC}$ value. The measured $J_{SC}$ values of the OPVs with MoO3/Al, HAT-CN/MoO3/Al, and MoO3/HAT-CN/Al at 0.7 V are 1.72, 1.01, and 2.06 mA cm$^{-2}$, respectively. Such changes in the device performance by the variation in the deposition sequence of the dual-anode buffer layer have also been observed in previous literature reports [11,12]. These results clearly indicate that the HAT-CN/MoO3/Al anode system differs from the MoO3/Al and MoO3/HAT-CN/Al anode systems.

Figure 3 shows the $C$-$V$ and $C$-$V$ characteristics of the inverted OPVs with MoO3/Al, HAT-CN/MoO3/Al, and MoO3/HAT-CN/Al anode systems. The $C$-$V$ characteristics are similar to the $J$-$V$ characteristics shown in Fig. 2. At 0.7 V, the OPV with HAT-CN/MoO3/Al records the lowest $C$ value, while the OPVs with MoO3/Al and MoO3/HAT-CN/Al show similar $C$ values. These low $J$ and $C$ values for the OPV with HAT-CN/MoO3/Al can be attributed to the low built-in potential ($V_b$). From the Mott-Schottky plot, the $V_b$ value is evaluated using the following equation:

$$C^{-2} = \frac{2}{\varepsilon q A N_D} \left( V_b - V \right)$$  

where $q$ is the elementary charge, $A$ is the area, $\varepsilon$ is the permittivity, and $N_D$ is the doping concentration [18]. Thus, the $x$-intercept of the Mott-Schottky plot provides the $V_b$ value across the device. Through a linear fitting, an identical $V_b$ value of 0.31 V is obtained for the OPVs with MoO3/Al and MoO3/HAT-CN/Al. However, the OPV with HAT-CN/MoO3/Al shows a $V_b$ of 0.27 V. This $V_b$ difference matches well with the $V_{OC}$ difference in the OPVs. The $V_{OC}$ values of the OPVs with MoO3/Al and MoO3/HAT-CN/Al are identical, but that of the OPV with HAT-CN/MoO3/Al is lower by 0.05 V. Thus, the low $V_{OC}$ of the OPV with HAT-CN/MoO3/Al can be mainly attributed to the low $V_b$ formation [19,20]. In addition, the low $V_b$ can increase the interface recombination, which lowers the $J_{SC}$ value. The low $V_b$ indicates a high hole-injection barrier at the anode interface, which results in a low $J$ value in the OPVs under dark conditions [Fig. 2(b)]. In contrast, although the $V_b$ value is identical in both the OPVs with MoO3/Al and MoO3/HAT-CN/Al, the OPV with MoO3/HAT-CN/Al shows a high $J$ value at 0.7 V under dark conditions compared to that with MoO3/Al. One possible explanation is the formation of a charge-transfer complex between HAT-CN and Al. When Al is deposited on HAT-CN, a strong chemical reaction occurs between them, and its HOMO level exists close to the Fermi level [16]. This state can assist the hole transport from MoO3 to Al, thereby increasing the $J$ value.

Figure 4 shows the $J$-$V$ characteristics of hole-only devices with the MoO3/Al, HAT-CN/MoO3/Al, and MoO3/HAT-CN/Al anode systems. Through the anode buffer layer, the hole transport direction is from Al to P3HT. Similar to the $J$-$V$ characteristics of the OPVs under dark conditions, the device with MoO3/HAT-CN/Al shows the highest $J$ value at 5 V, and that with HAT-CN/MoO3/Al shows the lowest $J$ value among the devices. The measured $J$ values of the hole-only devices with MoO3/Al, HAT-CN/MoO3/Al, and MoO3/HAT-CN/Al at 5 V are 169.1, 131.6, and 185.0 mA cm$^{-2}$, respectively. This also indicates the low $V_b$ formation by the HAT-CN/MoO3/Al anode

| Anode system | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF (%) | PCE (%) |
|--------------|-------------------------|-------------|-------|--------|
| MoO3/Al      | 10.60 ± 0.34            | 0.63 ± 0.004| 56.6 ± 2.12 | 3.74 ± 0.20 |
| HAT-CN/MoO3/Al | 10.28 ± 0.34          | 0.58 ± 0.008| 53.1 ± 1.38 | 3.19 ± 0.12 |
| MoO3/HAT-CN/Al | 11.40 ± 0.32         | 0.63 ± 0.005| 55.6 ± 1.38 | 3.97 ± 0.12 |

Figure 3. (Color online) $C$-$V$ (left axis, filled symbol) and $C$-$V$ (right axis, hollow symbol) characteristics of the inverted OPVs with MoO3/Al (black square), HAT-CN/MoO3/Al (red circle), and MoO3/HAT-CN/Al (blue triangle) anode systems under dark conditions.
system. Thus, the deposition sequence in the dual-anode buffer layer can significantly affect the device performance.

IV. Conclusion

In this study, the effect of deposition sequence in a MoO3 and HAT-CN dual-anode buffer layer on inverted OPVs is investigated. When HAT-CN is deposited prior to MoO3, the device performance of the OPV significantly deteriorates compared to that with a single MoO3 anode buffer layer. From the Mott-Schottky plots, it is concluded that the low PCE of the OPVs with HAT-CN/MoO3/Al is attributed to the low $V_{bi}$. However, when MoO3 is deposited prior to HAT-CN, the OPVs show a slightly higher PCE than that with a single MoO3 anode buffer layer. Thus, although MoO3 and HAT-CN have similar electronic structures, the deposition sequence in the dual-anode buffer layer significantly influences the device performance of the inverted OPVs.

Acknowledgements

This study was supported by the National Research Foundation of Korea (NRF-2018R1D1A1B07051050 and 2018R1A6A1A03025582) and Supporting Business for College Innovation from Kangwon National University.

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