

Sodium Doping at CuPc/C60 Interface for Photovoltaic Application

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1. Introduction

Interfacial engineering has become the most important aspect of the development of organic photovoltaics (OPVs) with high efficiencies. Small molecular OPVs with CuPc/C60 as an active layer have achieved power conversion efficiencies (PCE) of ~4%. The rapid improvement of PCE comes from in-depth understanding of the properties of the organic-metal and organic - organic interface.¹⁻⁵ The fundamental physics of the metal-organic interface have been extensively applied to improve OPVs and organic light-emitting devices. Most organic-organic donor-acceptor (D-A) interfaces have very small vacuum level offset, owing to their electronic wave functions are weakly coupled. Therefore, energy-level alignment at organic-organic interfaces has been studied less than that at metal-organic interfaces.

Alkali metal doped CuPc has been reported to have marked energy level shifts.⁶⁻¹⁰ When the C60 is deposited on the CuPc that is doped with alkaline metal, interfacial dipoles form; the Fermi level shifts toward the lowest unoccupied molecular orbital (LUMO) of CuPc; the potential difference between highest occupied molecular orbital (HOMO)-CuPc and LUMO-C60 increased upon doping with potassium, indicating a possible increase in the open-voltage of OPVs. Moreover, the alkali metal forms n-type dopant in C60 films, enhancing the electrical conductivity.¹¹⁻¹² These facts make the studies of the alkali doped CuPc/C60 became potential for the application in photovoltaics.

This letter reports on the photovoltaic behaviors of CuPc/C60-based solar cells by incorporating Na at the donor-acceptor (D-A) interface. The research is novel and important because the PCE was doubled when little Na was doped at the D-A interface and the device was post-annealed (75 °C, 40 min). The effects of thermal annealing of the Na-doped devices were systematically studied. The transport behaviors of electron/hole only devices were measured, indicating that the ratio of electron/hole mobility became unity when thermal annealing was performed. Capacitance-voltage relation of the device with and without Na doping was measured, revealing that the Na doping reduced the depletion depth because of the formation of the interfacial dipoles.

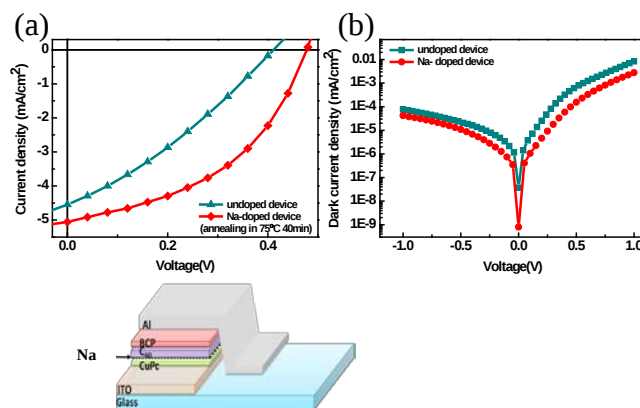


Fig.1. (a) *J-V* characteristics under AM1.5 simulated solar light illumination, and (b) dark *J-V* characteristics for un-doped (green) and Na-doped (red) device. Inset schematically depicts device structure.

2. Experimental details

Solar cell devices were fabricated on indium tin oxide (ITO) glass, each with an area of 1.7×1.25 cm². CuPc, Na, C60, BCP, and Al were deposited on the ITO glass in sequence using an evaporator in a vacuum (~3×10⁻⁶ Torr). The deposition rate of Na was as low as 0.01 Å/s, which was controlled by the heating current of the getter source. The devices were fabricated within either the glove box or the evaporator without exposure to air. The electron and hole only devices were fabricated by inserting MoO₃ and Cs₂CO₃ layers, respectively. The current-voltage relation under irradiation was recorded by Keithley 2600, and the capacitance-voltage relation was measured by Agilent E4980A.

3. Discussions

Figures 1(a) and 1(b) shows the *J-V* characteristics of the un-doped and Na-doped devices, respectively. It revealed that the open-circuit voltage (*V*_{oc}), short-circuit current (*J*_{sc}) increased apparently by the Na doping. Furthermore, the leakage current for Na -doped device declined.

Figures 2(a)–2(f) show the properties of OPVs with various Na contents. *V*_{oc}, *J*_{sc}, FF and PCE of the as-prepared samples slightly increased when they were slightly doped with Na (Na_xCuPc, *x*<0.2). PCE of the Na-doped device that was post-annealed for 40 minutes was doubled than the un-doped one. However, the performance of the devices declined as the annealing time was increased (>40 min) or the doping content was too heavy.

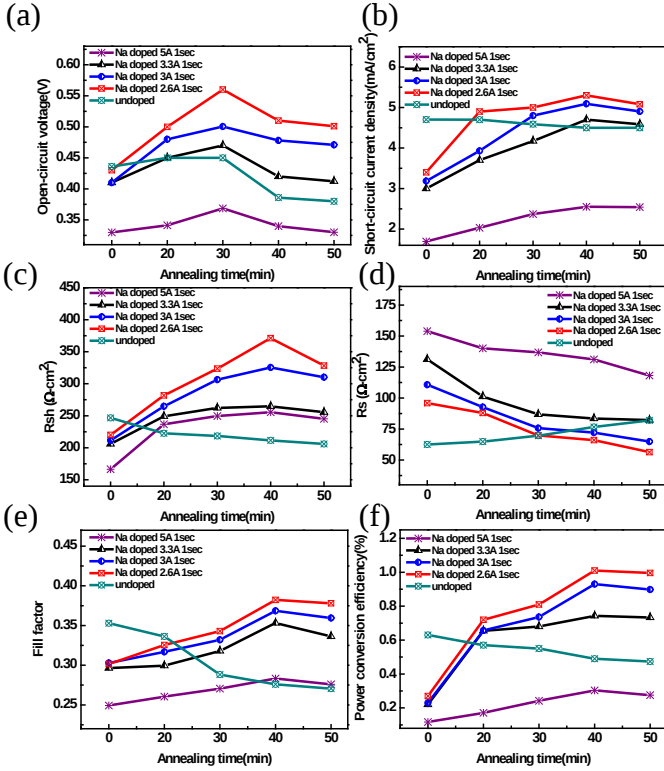


FIG.2. variation in (a) open-circuit voltage (Voc), (b) short-circuit current density (Jsc), (c) sheet resistance (Rsh), (d) series resistance (Rs), (e) FF, and (f) device efficiency (PCE) with various Na contents and annealing.

Figures 3 shows the mobilities of electron and hole, based on the space charge limited current (SCLC) model.¹³ The Na-doped and 40-min-annealed sample showed the mobility ratio (μ_h/μ_e) approach unity, which gives rise to the balance of carrier transport and reduces the effect of space charge. The short current increased, indicating that the doping of sodium at the D-A interface improves the carrier transport and properties of device.

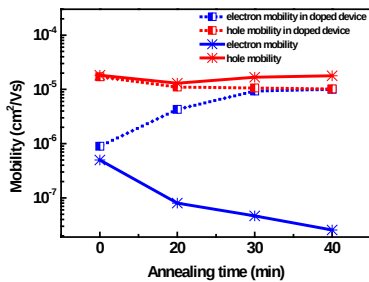


FIG.3. the mobility measurement in un-doped(solid line) and doped-Na(dot line) device at different annealing time.

Figures 4(a)-(b) plots the C-V curve at 100 kHz for undoped and Na-doped devices, respectively. The depletion capacitance of the Na-doped device decreased gradually with the post-annealing. Additionally, the junction capacitance of the Na-doped device was larger than the un-doped one, indicating the formation of the interfacial dipole by the interfacial doping. C-V depth-profiling also indicated that the interfacial doped Na diffused toward the

C60 side, which resulted in a small vacuum level offset at the interface. Therefore, the existence of the interfacial dipole contributed to the carrier transport, leading the doped devices superior to those without doping.

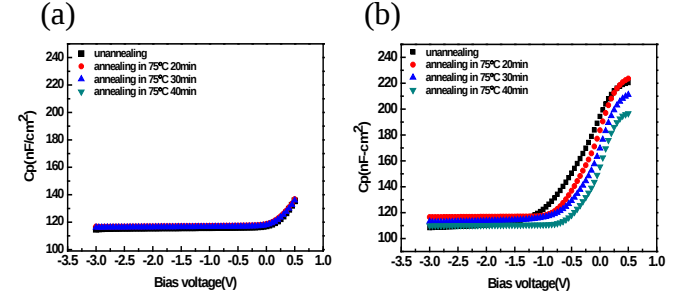


FIG.4 plots the capacitance-voltage (C-V) relationships that were measured at 100 kHz for CuPc/ Na /C60-based devices that were annealed under various annealing conditions.

4. Conclusion

The photovoltaic behaviors of CuPc/ C60-based solar cells upon incorporation of Na at the D-A interface were studied. PCE doubled when the device was doped with Na and post-annealed (75 °C, 40 min). Changes in binding energies, depletion capacitance, and electron and hole mobilities indicated existence of interfacial dipoles and modification of the electronic structures near the D-A interface. The substantial improvement of PCE was caused by the increase in Voc and Jsc, resulting from the modified charge transfer process and balance between the mobilities of electrons and holes. Finally, we suggest that other alkaline metals may similarly improve the cell efficiency.

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