Relationship between indium tin oxide surface treatment and hole injection in C60 modified devices

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(Received 4 September 2006; accepted 13 November 2006; published online 19 December 2006)

The effect of indium tin oxide (ITO) surface treatment on hole injection in organic light-emitting diode with C60 as a buffer layer on ITO was studied. Double surface dipole layer was induced on oxygen plasma treated ITO surface, while no dipole formation was observed on ITO without surface treatment. Interfacial energy barrier between ITO and hole transport layer was reduced by 0.4 eV by C60 modification on oxygen plasma treated ITO surface, while there was no change of interfacial energy barrier by C60 on ITO without surface treatment. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2410224]

C60 has been known as a *n*-type semiconductor and has long been used as a moderately strong electron acceptor in solar cells.[1,2] Charge transfer from inorganic or metal to C60 can be easily induced and it can accept up to six electrons. In addition, it has a high electron mobility of 1 $cm^2/V\,s$ even though hole mobility is relatively low compared with other organic hole transport materials.[3]

Therefore, there have been several studies about using C60 as an electron transport layer or modifier for electrodes. Feng *et al.* reported that C60 could give a low driving voltage and Ohmic contact formation between C60 and LiF/Al.[4] Hong *et al.* used C60 as a buffer layer on indium tin oxide (ITO) and the interfacial energy barrier between ITO and *N*, *N*'-di(1-naphthyl)-*N*, *N*'-diphenylbenzidine (NPB) was reduced by 0.5 eV by surface dipole formation.[5] Our group applied C60 as a buffer layer on Al electrode and observed 0.9 eV decrease of interfacial energy barrier.[6] Current density was increased by C60 buffer layer on Al and current efficiency was also improved by efficient hole injection from Al to light-emitting layer. Other than these, there have been other works about using C60 as a dopant for hole transport layer.[7,8]

In this work, we investigated the relationship between ITO surface treatment and hole injection in C60 modified devices. Hole injection from ITO to NPB was correlated with surface treatment and C60 buffer layer and hole injection mechanism in C60 modified devices was clarified.

Device configurations of ITO/NPB(100 nm)/Al and ITO/C60/NPB(100 nm)/Al were used to study hole injection from ITO to NPB. C60 was evaporated at a deposition rate of 0.1 Å/s and NPB was evaporated at an evaporation rate of 1 Å/s. ITO substrates were exposed to oxygen plasma at a rf power of 100 W with O_2 flow rate of 50 SCCM (SCCM denotes cubic centimeter per minute at STP) after cleaning. Devices were encapsulated with glass lid and calcium oxide getter after organic and metal deposition. Current-voltage (*I-V*) characteristics of the devices were measured with keithley 0253A.

C60 is an intrinsically nonpolar molecule with 60 carbon atoms on the spherical surface. However, it is a strong electron acceptor and can form a charge transfer complex with metals, leading to interfacial dipole formation between metal and C60.[9] Hayashi *et al.* reported that the vacuum level of metals such as Au, Cu, and Ag was affected by deposition of C60 and it induced interfacial dipole formation due to strong interaction between metals and C60. There has been another study about the interaction between oxide and C60,[5] but the study could not give information about the relationship between ITO surface properties and hole injection in C60 modified devices. Therefore, hole injection in C60 modified devices was correlated with ITO surface treatment and detailed mechanism of hole injection was elucidated in this work.

To study the hole injection through ITO-C60 interface, *I-V* characteristics of devices were measured. Figure 1 shows *I-V* characteristics of four devices with different interface properties between ITO and NPB. Hole only devices without any surface treatment did not show any difference between

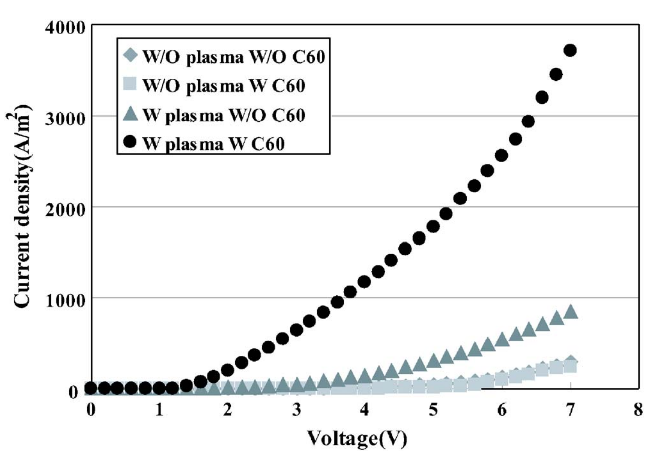

FIG. 1. Current density–voltage curves of C60 modified device with and without O_2 plasma treatment.

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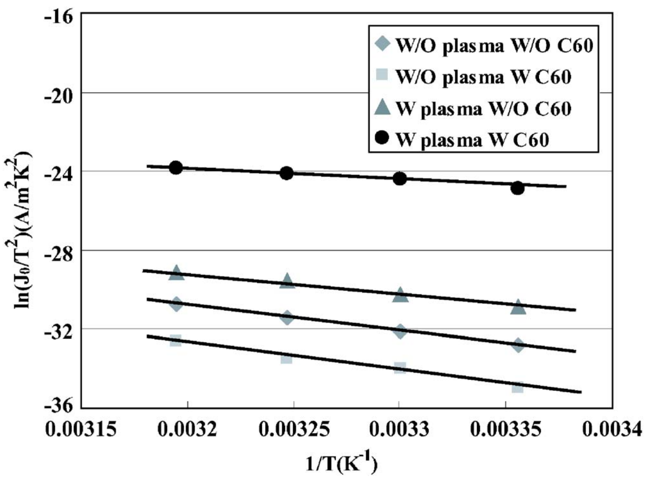

FIG. 2. Plot of field-free current density against inverse temperature of C60 modified devices with and without O_2 plasma treatment.

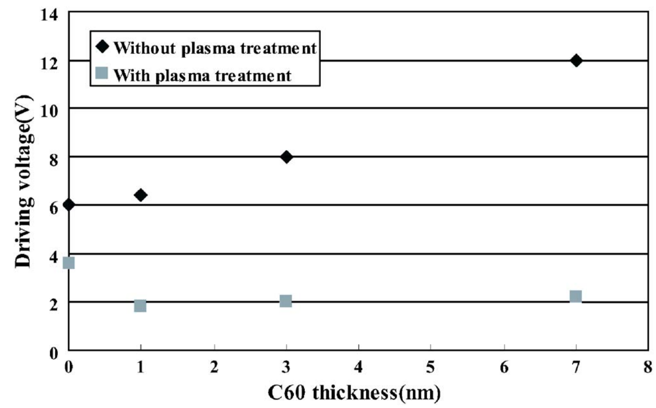

FIG. 4. Plot of driving voltage of C60 modified devices at 100 A/m^2 according to thickness of C60.

C60 free device and C60 modified device, while a large increase of current density by C60 was observed in O_2 plasma treated devices. This result indicates that hole injection of C60 modified devices is greatly dependent on surface properties of ITO. To get more information about the hole injection of C60 modified devices, the interfacial energy barrier between ITO and NPB was calculated from temperature dependence of field-free current density. Current density in hole only devices is known to be expressed by the following equation proposed by Matsumura *et al.*:[10]

$$J = J_0 \exp\{q[q(V - V_{bi})/4\pi\varepsilon\varepsilon_0 d]^{1/2}\}/kT, \tag{1}$$

$$J_0 = A^* T^2 \exp(-q\phi_b/kT). \tag{2}$$

J is the current density, J_0 is the field-free current density, q is the electrical charge of an electron, V_{bi} is the built-in voltage due to the difference between work functions of electrodes, ε is a relative dielectric constant of medium, ε_0 is a dielectric constant of vacuum, d is the thickness of NPB layer, ϕ_b is the energy barrier, k is the Boltzmann constant, and T is the temperature. A linear relationship between $\ln J$ and $(V - V_{bi})^{1/2}$ was obtained, indicating that hole injection from ITO to NPB can be regarded as Schottky emission and can be expressed by Eq. (1). Interfacial energy barrier (ϕ_b) was calculated from the plot of $\ln J_0/T^2$ against T^{-1} as a slope of linear regression and it is shown in Fig. 2. C60 modification reduced the energy barrier between ITO and NPB by 0.4 eV on O_2 plasma treated ITO, while there was no change of energy barrier by C60 buffer layer on bare ITO. It is well known that O_2 plasma treatment of ITO can induce surface dipole on ITO due to formation of negatively charge oxygen or tin and removal of surface carbon contamination,[11,12] while bare ITO has high carbon content on the surface and little dipole formation. C60 is an intrinsically nonpolar molecule with low dipole moment even though it can accept electrons very easily through charge transfer. Therefore, it is difficult to induce surface dipole on bare ITO by C60 modification, while surface dipole can be readily induced on O_2 plasma treated ITO. Surface dipole formation by C60 on O_2 plasma treated ITO is schematically described in Fig. 3. The low energy barrier in C60 modified ITO can be explained by a double surface dipole model. The first surface dipole formation is induced on ITO by O_2 plasma treatment and the second dipole is induced by C60. The surface dipole formation by C60 is originated from charge transfer from the first dipole layer to C60 because uniform electron distribution is deformed by polar O_2 plasma treated ITO. Compared with O_2 plasma treated ITO, bare ITO has little surface dipole to help charge transfer from ITO to C60 which is intrinsically a nonpolar molecule. Therefore, no dipole formation is observed on bare ITO after C60 modification, resulting in no change of energy barrier after C60 modification.

To get more information on the hole injection in C60 modified devices, the driving voltage of C60 modified devices was monitored according to the thickness of C60 layer. Figure 4 is the plot of the driving voltage of hole only devices at 100 A/m^2 against C60 thickness. The driving voltage of C60 modified devices was increased without O_2 plasma treatment, while it was decreased after O_2 plasma treatment even though it was increased at high C60 thickness. The reduced driving voltage of C60 modified devices after O_2 plasma treatment is due to the low interfacial energy barrier which was induced by surface dipole formation. The low interfacial energy barrier facilitates hole injection from ITO to NPB and gives low driving voltage. However, C60 has a low hole mobility of 10^{-4} cm^2/V s and hole injection is

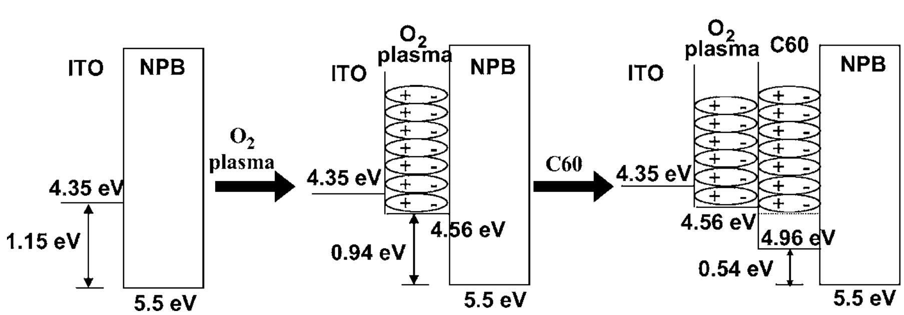

FIG. 3. Schematic diagram for dipole formation in C60 modified devices with O_2 plasma treatment.

delayed at high C60 thickness. Compared with O_2 plasma treated devices, the driving voltage of C60 devices was increased according to C60 thickness without O_2 plasma treatment. There was no interfacial energy barrier reduction by C60 on bare ITO, leading to no change of driving voltage by C60 modification. Instead, the driving voltage was gradually increased by C60 due to low hole mobility of C60.

In summary, hole injection of C60 modified devices were greatly dependent on surface properties of ITO. O_2 plasma treatment was effective to induce surface dipole by C60, while surface dipole was not induced by C60 modification on bare ITO. The surface dipole formation by C60 on O_2 plasma treated ITO reduced interfacial energy barrier by 0.4 eV, resulting in low driving voltage.

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