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LETTERS

Insertion of Thin Interlayers under the Negative Electrode of C_{60} Schottky-Type Photovoltaic Cells

Tetsuya Taima,[†] Masayuki Chikamatsu, Raghu Nath Bera, Yuji Yoshida, Kazuhiro Saito,* and Kiyoshi Yase

Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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Although C_{60} is known as a typical n-type organic semiconductor, Schottky-type cells of an ITO/C_{60}/Al structure do not show definite photovoltaic effects. Thin metallic interlayers were inserted at the C_{60}/Al interface to examine enhancement of the power conversion efficiency in the cells. An ITO/C_{60}/Mg/Al cell showed an efficiency up to 0.15% for AM1.5, which is the largest efficiency in the Schottky-type cells of n-type organic semiconductors. The improvement of the photovoltaic effects seems to be caused by intercalation of Mg into C_{60} layer as a dopant.

Introduction

The number of studies concerning organic solar cells with thin films of organic semiconductors is increasing because of their potential low cost and simple fabrication processes.[1−4] However, there is no organic solar cell that has enough power conversion efficiency for practical usage yet, because n-type organic semiconductors did not exhibit sufficient semiconducting properties. For n-type organic semiconductors, O_2 gas in air behaves as an electron acceptor to decrease their carrier density, whereas it behaves as a hole dopant for p-type organic semiconductors. Although C_{60} is a well-known n-type organic semiconductor, Schottky-type cells of C_{60} have not shown definite photovoltaic effects. Recently, several research groups have reported that insertion of thin interlayers under the negative electrode of organic thin film devices is effective to improve their performance.[5−7] Schottky-type photovoltaic cells, which have a simple structure, are convenient to investigate such effects.[8,9] In the present work, we study the influence of the insertion of thin metallic layer for C_{60} Schottky-type solar cells.

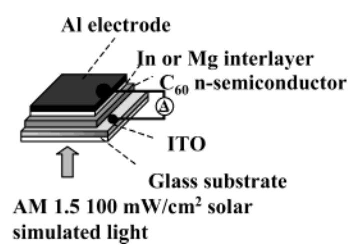

Figure 1. Schematic of the layered structure of the Schottky-type solar cell and arrangement for measurement of $J-V$ characteristics.

Experimental Section

Figure 1 shows a structure of C_{60} Schottky-type solar cells used in this study. We fabricated three types of cells, i.e., with In interlayer, with Mg interlayer, and without interlayer as a control. The Schottky barrier is formed at the ITO/C_{60} interface; on the other side, ohmic contact is formed at the C_{60}/metallic electrode interface.

* Corresponding author. E-mail: kazuhiro-saito@aist.go.jp. Tel: +81-29-861-6252. Fax: +81-29-861-6303.
[†] E-mail: tetsuya-taima@aist.go.jp.

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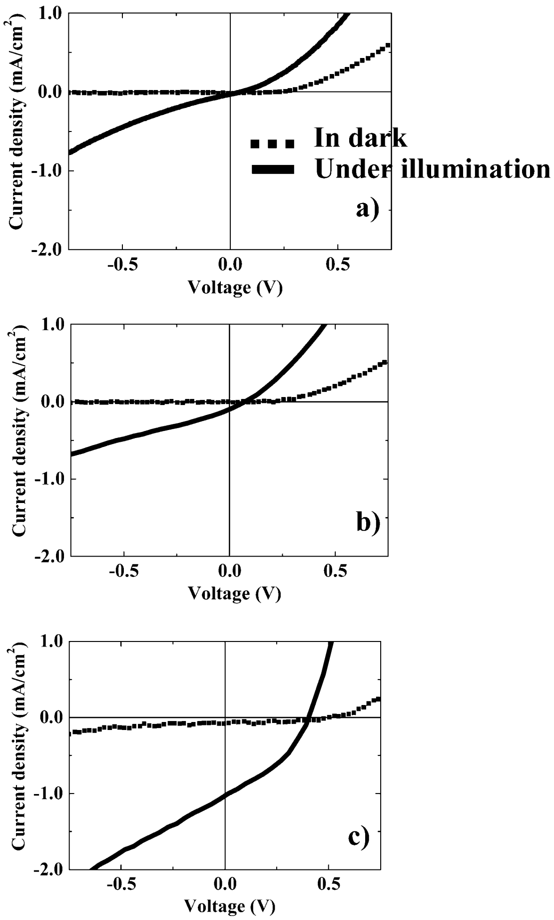

Figure 2. $J-V$ characteristics in the dark (dotted line) and under the illumination of AM1.5 (solid line): (a) ITO/C_{60}/Al cell; (b) ITO/C60/In/Al cell; (c) ITO/ C_{60}/Mg/Al cell.

C_{60} film was deposited by vacuum evaporation at 10^{-7} Torr, which thickness was approximately 100 nm, after the glass substrate with an ITO electrode was cleaned by UV/O_3 cleaner. In/Al, Mg/Al, or Al electrodes were deposited onto the surface of C_{60} layer by vacuum evaporation at 10^{-6} Torr. The thicknesses of the Al electrode and the insertion layers were approximately 100 and 10 nm, respectively. The active area of the devices was 4 mm^2.

Current density versus voltage ($J-V$) characteristics of the cells was measured in dark or under illumination of AM 1.5 (100 mW/cm^2), as shown in Figure 1 at room temperature in air. Action spectra of the short-circuit photocurrent (I_{sc}) were also measured at room temperature in air. The cells were illuminated through the substrate and ITO base with monochromatic light of 100 μW/cm^2. The wavelength of the incident light was changed by a monochromator.

Results and Discussion

Typical $J-V$ characteristics of the cells in dark and under illumination are shown in Figure 2. Open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), power conversion efficiency (η) of the cells and work functions of the metals are listed in Table 1. Solar cell parameters of C_{60} Schottky-type cells have not been reported so far. In fact, the ITO/C_{60}/Al cell did not show definite V_{oc} and J_{sc}. In contrast to the cells of ITO/C_{60}/Al and ITO/C_{60}/In/Al structures, the ITO/C_{60}/Mg/Al cell exhibits remarkable values. It should be noted that the power conversion efficiency of the ITO/C_{60}/Mg/Al cell was up to 0.15%, which is the largest efficiency in the Schottky-type cells of n-type organic semiconductors.

TABLE 1: Solar Cell Parameters of the Cells and Work Functions of the Metals

	ITO/C_{60}/Al	ITO/C_{60}/In/Al	ITO/C_{60}/Mg/Al
work function	4.28	4.12	3.66
V_{oc} (V)	0.046	0.07	0.40
J_{sc} (mA/cm^2)	2.77×10^2	0.103	1.04
fill factor		0.19	0.4
efficiency η (%)	$<10^4$	0.001	0.15

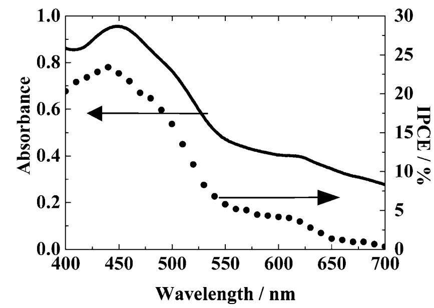

Figure 3. Absorption spectrum of a C_{60} film (solid line) and IPCE spectrum of an ITO/C_{60}/Mg/Al cell under the illumination of 100 μW/cm^2 monochromic light (dotted line).

The measured action spectrum of I_{sc} was converted into the spectrum of incident photon to converted electron efficiency (IPCE) by the following equation:

$$\text{IPCE (\%)} = \frac{1240}{\lambda\ (\text{nm})} \frac{I_{sc}\ (\mu\text{A/cm}^2)}{I_{inc}\ (\text{W/m}^2)} \tag{1}$$

where λ and I_{inc} are wavelength and intensity of incident light, respectively. Figure 3 shows an optical absorption spectrum of a C_{60} film and an IPCE spectrum of an ITO/C_{60}/Mg/Al cell. IPCE spectra of ITO/C_{60}/Al and ITO/C_{60}/In/Al cells were impossible to measure, because the magnitude of I_{sc} was too low to detect for the present system. The IPCE spectrum is similar to the absorption spectrum. So we could conclude that the charge separation region of this device was not at the C_{60}/Mg interface but at the ITO/C_{60} interface, because the inner-filter effect was not observed in the cell. Furthermore, the similarity suggests that insertion of the Mg layer did not cause drastic change in absorption spectra of the C_{60} layer. It is worthwhile to notice that the IPCE at around 450 nm reaches almost 30% despite the low absorption coefficient in the C_{60} layer. C_{60} does not possess a strong absorption band in the visible region, because optical transition between the LUMO and HOMO is forbidden because of its high symmetry. If the cells are sensitized by introduction of dyes, they will show higher η.[10]

Here we should discuss why photovoltaic effects in the ITO/C_{60}/Mg/Al cell was dramatically enhanced in comparison with the ITO/C_{60}/Al and the ITO/C_{60}/In/Al cells. When the contact resistance at the C_{60}/metal electrode or the conductivity in the C_{60} layer is improved, FF and J_{sc} will increase. It has been reported that alkali and alkaline-earth metals are easily intercalated into C_{60} film during deposition in a vacuum.[11,12] Doping effects for C_{60} have been heavily investigated in the field of organic superconductors so far. For example, Ca-, Sr-, or Ba-doped C_{60} films exhibit superconductivities. On the other hand, Mg-doped C_{60} films exhibit semiconducting properties, and they are expected to exhibit high performance as an n-type organic semiconductor.[13−15] Therefore, Mg doping for the C_{60} layer is going to occur by insertion of the Mg layer. In fact, the remarkable increase in V_{oc} of the ITO/C_{60}/Mg/Al cell suggests a change in Fermi level of the C_{60} layer due to an increase in carrier concentration by the doping effect.

Another possible origin of the enhancement is change in work function of the negative electrode due to the interlayer. As shown in Table 1, the relations among work functions of the metals and J_{sc} of the cells are Mg < In < Al and ITO/C_{60}/Mg/Al > ITO/C_{60}/In/Al > ITO/C_{60}/Al, respectively. The correlation of work function with η suggests that the contact resistance at the C_{60}/metal electrode is strongly influenced by the work function. If an ideal ohmic contact is not formed at the interface, a photovoltaic effect, which cancels out the V_{oc}, will occur. Similar correlation of the work function with quantum efficiency is also reported in OLEDs on the basis of the analysis of carrier injection efficiency at the organic semiconductor/negative electrode interface.[5]

In summary, alkaline-earth metal Mg plays an important role in the improvement of electron transportation in the C_{60} layer. We succeeded in improving the C_{60} layer as an n-type organic semiconductor using simple method, i.e., insertion of a thin Mg layer under the negative electrode. This C_{60}/Mg combination is valuable not only for organic solar cells but also for other organic devices, such as OLEDs or organic TFTs, which lack a high-performance n-type semiconductor.

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