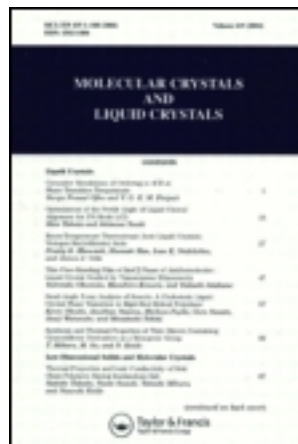


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Evaluation of Barrier Width by Low-Frequency Capacitance Measurements for MoO₃-doped p-Type C₆₀ Films

Tadashi Yoshioka^{a b}, Masayuki Kubo^{a b}, Norihiro Ishiyama^{a b c},
Toshihiko Kaji^{a b c} & Masahiro Hiramoto^{a b c}

^a Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki, Aichi, Japan

^b JST, CREST, 5, Sanbancho, Chiyoda-ku, Tokyo, Japan

^c The Graduate University for Advanced Studies, 5-1 Higashiyama, Myodaiji, Okazaki, Aichi, Japan

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Evaluation of Barrier Width by Low-Frequency Capacitance Measurements for MoO₃-doped *p*-Type C₆₀ Films

TADASHI YOSHIOKA,^{1,2,*} MASAYUKI KUBO,^{1,2}
NORIHIRO ISHIYAMA,^{1,2,3} TOSHIHIKO KAJI,^{1,2,3}
AND MASAHIRO HIRAMOTO^{1,2,3}

¹Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki, Aichi, Japan

²JST, CREST, 5, Sanbancho, Chiyoda-ku, Tokyo, Japan

³The Graduate University for Advanced Studies, 5-1 Higashiyama, Myodaiji, Okazaki, Aichi, Japan

*The Schottky barrier width (W_{dep}) formed at MoO₃-doped *p*-type C₆₀/Ag interface was evaluated by low-frequency capacitance measurements. At relatively low-doped concentration of 3000 ppm, W_{dep} was determined to 57 nm and the clear rectification behavior was observed. On the other hand, at heavily-doped concentration of 10000 ppm, W_{dep} shrunk to 23 nm and the quasi-ohmic behavior due to the tunneling current was observed. Heavy doping technique can be applied to the fabrication of ohmic C₆₀/metal contact.*

Keywords Low-frequency capacitance measurements; MoO₃-doped *p*-type C₆₀; *pn*-control; Schottky barrier parameters

Introduction

Organic solar cells consisting of vacuum-deposited small-molecular thin films have been intensively studied [1–6]. Fullerene (C₆₀) is an indispensable organic semiconductor for solar cell application. By using highly-purified ‘seven-nines’ C₆₀, 1 μm-thick cells showing the short-circuit photocurrent density of 20 mAcm^{−2} and efficiency of 5.3% was fabricated [7,8].

pn-control for highly-purified semiconductors by adding small amounts of dopants is important to improve the performance of organic solar cells. We have reported *pn*-control of C₆₀ films from *n*- to *p*-type by doping with MoO₃ [9,10]. Upwardly bent Schottky junction was confirmed to be formed at the *p*-type C₆₀/Ag contact by means of the Kelvin vibrating capacitor and the photovoltaic measurements [9].

Determination of Schottky barrier parameters, i.e., the carrier concentration (N), depletion layer width (W_{dep}), and built-in potential (V_{bi}), is indispensable to control the characteristics of the metal /organic semiconductor contacts.

*Address correspondence to Tadashi Yoshioka, Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki 444-8787, Aichi, Japan. Tel./ Fax: +81-564-59-5537; E-mail: tadashi@ims.ac.jp

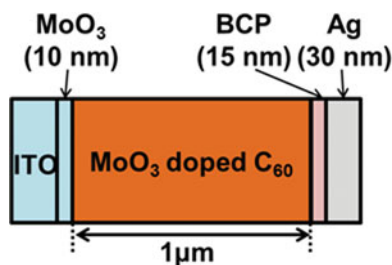


Figure 1. Sandwich-type cell. *p*-type Schottky junction is formed at MoO₃-doped C₆₀/Ag interface. BCP is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline also known as bathocuproine.

In this study, we applied the low-frequency capacitance measurements [11] to determine the parameters of Schottky junction formed between *p*-type MoO₃-doped C₆₀ and Ag electrode.

Experimental

C₆₀ sample (Frontier Carbon, nanom purple TL) was purified by single crystal-formed sublimation under 1 atm of N₂ [12]. The purity of the C₆₀ crystals was determined to be 7N (99.99999%) [7,8]. As an acceptor dopant, MoO₃ (Alfa Aesar, 99.9995%) was used. The cell structure is shown in Fig. 1. All films were deposited on ITO glass substrates under 10⁻⁵ Pa. The cell area was 0.06 cm². MoO₃ doping was carried out by the co-evaporation.

Low-frequency capacitance measurements [11] were performed under vacuum condition (10⁻³ Pa). A periodical triangular bias was applied to the cell by using a function generator (Hokuto Denko, HB-102) and dark current was measured by a picoammeter (Keithley 485).

Results

Dark current-voltage curve under the scanning speed of 7 V/s for the MoO₃ doping concentration of 3000 ppm is shown Fig. 2. Clear hysteresis was observed. Differential capacitance

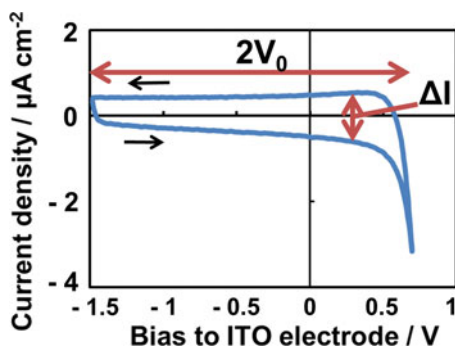


Figure 2. Dark current-voltage curve for MoO₃ (3000 ppm)-doped C₆₀ cell. Clear hysteresis was observed at the scan rate of 7 V/s.

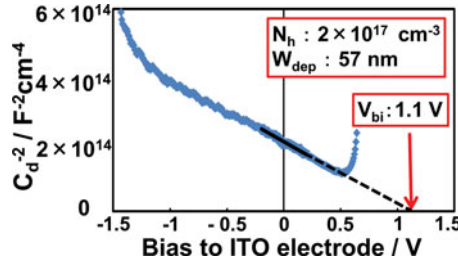


Figure 3. Mott-Schottky plot for MoO₃ (3000 ppm)-doped C₆₀ cell.

(C_d(V)) can be obtained by Eq. (1).

$$C_d(V) = \Delta I(V) / 8V_0 f. \quad (1)$$

Here, $\Delta I(V)$, $2V_0$, and f are the current difference due to the hysteresis, the range of the applied bias, and the frequency of periodical triangular bias, respectively.

Figure 3 shows the Mott-Schottky plot ($C_d^{-2} - V$) obtained from the curve in Fig. 2. Clear linear relationship was observed (broken line). From the slope, carrier concentration for holes (N_h) was determined to be $2 \times 10^{17} \text{ cm}^{-3}$ based on the Eq. (2) and on the relative dielectric constant (ϵ) of 4.4 for C₆₀ [13].

$$C_d^{-2}(V) = 2(V - V_{bi}) / eN\epsilon\epsilon_0. \quad (2)$$

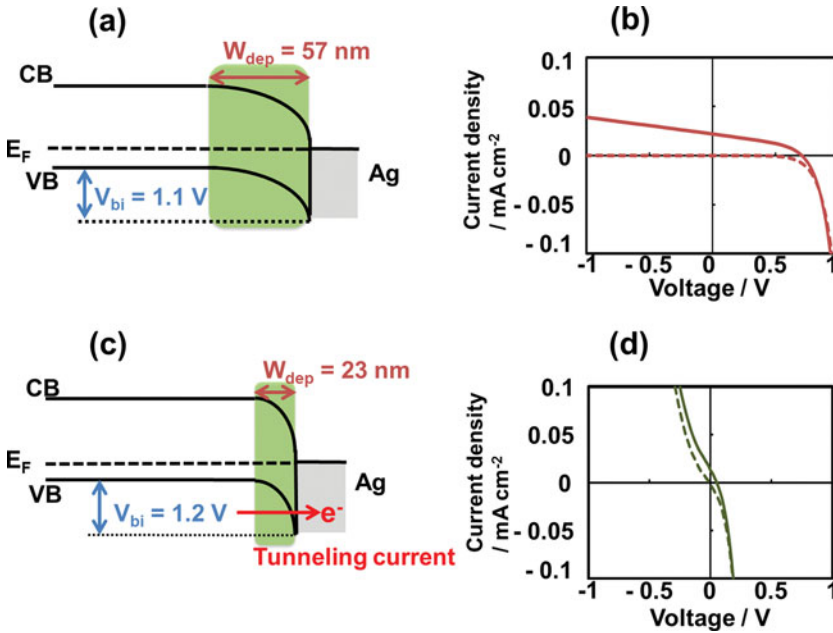


Figure 4. Energy structures and current-voltage characteristics for 3000 ppm (a) and (b) and 10000 ppm (c) and (d) MoO₃-doped C₆₀ cells. Photocurrent and dark current are shown by solid and broken curves, respectively.

From the C_d value at zero bias ($V = 0$), depletion layer width (W_{dep}) was determined to be 57 nm based on the Eq. (3)

$$C_d(V = 0) = \varepsilon \varepsilon_0 / W_{\text{dep}}. \quad (3)$$

When MoO_3 concentration was increased to 10000 ppm, larger N_h value of $9 \times 10^{17} \text{ cm}^{-3}$ and thinner W_{dep} value of 23 nm were obtained.

Based on the obtained barrier parameters, energetic structures in Fig. 4(a) and (c) can be drawn [14]. In the case of the MoO_3 concentration of 3000 ppm (Fig. 4(b)), clear rectification behavior and photovoltaic property were observed. This means that the depletion layer at $p\text{-C}_{60}/\text{Ag}$ interface acts as the active layer for photocurrent generation. On the other hand, in the case of the MoO_3 concentration of 10000 ppm, *quasi*-ohmic behavior was observed (Fig. 4(d)). We think that the tunneling of carriers occurs due to the very thin width of the depletion layer (Fig. 4(c)).

Conclusion

We succeeded in controlling the energetic structure of Schottky junction at $p\text{-C}_{60}/\text{Ag}$ interface by changing the doping concentration of MoO_3 acceptor. Heavy doping technique offers the way to make ohmic $\text{C}_{60}/\text{metal}$ contact. Ohmic contacts formation of two metal/organic interfaces in organic solar cell would increase the fill factor by decreasing the cell resistance.

Acknowledgment

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References

- [1] Sun, S.-S., & Sariciftci, N. S. (2005). *Organic Photovoltaics, Mechanisms, Materials and Devices*, CRC Press, New York.
- [2] Spanggaard, H., & Krebs, F. C. (2004). *Sol. Energy Mater. Sol. Cells*, 83, 125.
- [3] Hoppe, H., & Sariciftci, N. S. (2004). *J. Mater. Res.*, 19, 1924.
- [4] Tang, C. W. (1986). *Appl. Phys. Lett.*, 48, 183.
- [5] Hiramoto, M., Fujiwara, H., & Yokoyama, M. (1991). *Appl. Phys. Lett.*, 58, 1062.
- [6] Hiramoto, M., Fujiwara, H., & Yokoyama, M. (1992). *J. Appl. Phys.*, 72, 3781.
- [7] Hiramoto, M., & Sakai, K. (2008). *Mol. Cryst. Liq. Cryst.*, 491, 284.
- [8] Hiramoto, M. (2008). *Proc. SPIE*, 7052, 70520H.
- [9] Kubo, M., Kaji, T., Iketaki, K., & Hiramoto, M. (2011). *Appl. Phys. Lett.*, 98, 073311.
- [10] Kubo, M., Kaji, T., & Hiramoto, M. (2011). *AIP Advances*, 1, 032177.
- [11] Twarowski, A. J., & Albrecht, A. C. (1979). *J. Chem. Phys.*, 70, 2255.
- [12] Laudise, R. A., Kloc, Ch., Simpkins, P. G., & Siegrist, T. (1998). *J. Cryst. Growth*, 187, 449.
- [13] Hebard, A. F., Hadon, R. C., Fleming, R. M., & Kortan, A. R. (1991). *Appl. Phys. Lett.*, 59, 2109.
- [14] For the ease of understanding, Figure 4 is depicted without BCP layer. The role of the BCP layer is to help Schottky barrier formation at the MoO_3 -doped p -type C_{60}/Ag interface. In the case of heavily doping of 10000 ppm, actually, the C_{60}/Ag interface acts as *quasi*-ohmic either with or without BCP.