J|A|C|S
COMMUNICATIONS

Published on Web 06/12/2003

Conductivity and Field Effect Transistor of $La_2@C_{80}$ Metallofullerene

Shin-ichiro Kobayashi,[†,‡] Satoshi Mori,[†] Satoru Iida,[†] Hiroaki Ando,[†] Taishi Takenobu,[†,‡] Yasujiro Taguchi,[†,‡] Akihiko Fujiwara,[‡,§] Atsushi Taninaka,[⊥] Hisanori Shinohara,[‡,⊥] and Yoshihiro Iwasa[†,‡]

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan, CREST, Japan Science and Technology Corporation, Kawaguchi 330-0012, Japan, Japan Advanced Institute of Science and Technology, Ishikawa 923-1292, Japan, and Department of Chemistry & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan

Received March 1, 2003; E-mail: iwasa@imr.edu

Endohedral metallofullerenes have recently attracted broad interests because of their exotic forms and novel molecular properties.[1] Various kinds of atoms can be encapsulated in a carbon cage, and in many cases, electrons are transferred from the encapsulated atoms to the carbon cage. Among them, $La_2@C_{80}$ is of particular importance[2] because of its icosahedral (I_h) symmetry, which is the same as that of the well-known C_{60} molecule, where high-symmetry played a crucial role in a large variety of interesting properties. Because of this unique molecular structure, much effort has been made to clarify the properties of $La_2@C_{80}$ molecule. According to a molecular orbital calculation,[3] six electrons in total are transferred from the two La atoms to the C_{80} cage, forming a stable closed-shell configuration described as $(La^{3+})_2@C_{80}{}^{6-}$. The highest occupied molecular orbital (HOMO) consists of nearly 4-fold degenerated π-orbitals of the fullerene cage, while the lowest unoccupied molecular orbital (LUMO) is mainly derived from an orbital of the La atom. An X-ray diffraction analysis[4] based on maximum-entropy/Rietveld method has confirmed that the La atoms are indeed encapsulated in the carbon cage and that the valence state of the La atoms is trivalent. The magnitude of the HOMO−LUMO gap of the molecule has been determined to be 0.87 and 1 eV by an electrochemical method[5] and optical absorption spectra on solution,[6] respectively. A very recent scanning tunneling spectroscopy experiment of $La_2@C_{80}$ on a hydrogen-terminated Si(100)-2 × 1 surface provides a bit larger gap of 1.3−1.5 eV.[7] These values are considerably smaller than that of C_{60}, possibly due to the enlarged cage size. Although $La_2@C_{80}$ has been extensively investigated as an individual molecule, solid-state properties still remain unknown because of the limited amount of materials. To overcome this difficulty, fabrication of thin films and their characterization are of crucial importance, since it does not require a large amount of source samples. Particularly, recently emerging techniques of organic transistors[8] are quite useful not only for practical application but also for fundamental characterization of molecular materials. In this Communication, we report the first demonstration of $La_2@C_{80}$ thin film field effect transistor and related properties, based on which discussion is given on the electronic states and carrier transport in $La_2@C_{80}$ film.

Soot containing $La_2@C_{80}$ dimetallofullerene and other La-based metallofullerenes was produced in a dc (300−400 A) spark mode under He flow at 50−80 Torr. $La_2@C_{80}$ was isolated by two-stage high-performance liquid chromatography (HPLC).[1] Laser desorption mass spectrometry and the HPLC analysis showed that the sample purity is more than 99.8%. $La_2@C_{80}$ films of 50 nm in thickness were prepared by vacuum deposition on glass substrate and subjected to conductivity and optical absorption measurements. The conductivity measurement was done by a two-probe method in a vacuum of less than 10^{-5} Torr from 150 to 450 K. We used a grating- (Fourier transform-) type spectrometer to measure optical absorption spectra above (below) 0.6 eV. For comparison, we also measured absorption spectra of $La_2@C_{80}$ in toluene solution. We fabricated a $La_2@C_{80}$ thin film transistor with a back gate configuration, which is schematically shown in the inset of Figure 2. The gate electrode was made of heavily doped *p*-type silicon, on top of which an insulating silicon-dioxide layer with 400 nm in thickness was grown by a thermal oxidation. Drain and source electrodes were made of Cr/Au by using a standard photolithography technique. The channel length and width were 50 μm and 2 mm, respectively. $La_2@C_{80}$ film of 10 nm in thickness was made by a molecular beam deposition at the base pressure below 10^{-9} Torr. After deposition, the sample was transferred to a characterization chamber without being exposed to air, and subsequently, the current−voltage characteristics were measured with three probes equipped with the high vacuum chamber.

We show, in the inset to Figure 1, optical absorption spectra of $La_2@C_{80}$ thin-film and toluene solution at room temperature. Absorption threshold for both spectra are about 0.5−0.6 eV, which is smaller than the value previously reported for the molecule.[6] A notable difference between the two spectra is that the first absorption band centered at 1.5 eV is stronger in intensity in the thin film than in the solution. Similar enhancement of absorption intensity upon the solid formation has long been well-known for C_{60}, where it is believed that a symmetry-forbidden intramolecular excitation becomes allowed as a charge-transfer type excitation from one molecule to the nearest neighbors.[9] The same activation of absorption band seems likely to happen in the present case.

Figure 1 depicts an Arrhenius plot of conductivity data. The value of σ at room temperature was somewhat sample dependent, ranging between the order of 10^{-3} and 10^{-5} S/cm. This value is comparable to that of $Dy@C_{82}$.[10] The σ of $La_2@C_{80}$ displayed an activation-type temperature dependence ($\sigma = \sigma_0 \exp(-\Delta/k_BT)$). The activation energy Δ was determined as $\Delta = 0.20$ eV from the fit to the data for the whole temperature range measured. It should be noted that the gap value $2\Delta = 0.39$ eV is close to the absorption edge 0.5 eV, found in the optical absorption spectrum of the film form in the inset of Figure 1, suggesting that the conductivity is attributed to the band-like transport of thermally activated carriers across the band gap 2Δ. However, this scenario is excluded by the following field effect measurement.

Figure 2 shows transistor characteristics, where the drain-source current (I_{DS}) is plotted against drain-source voltage (V_{DS}) for various

[†] Institute for Materials Research.
[‡] CREST, Japan Science and Technology Corporation.
[§] Japan Advanced Institute of Science and Technology.
[⊥] Nagoya University.

10.1021/ja034944a CCC: $25.00 © 2003 American Chemical Society

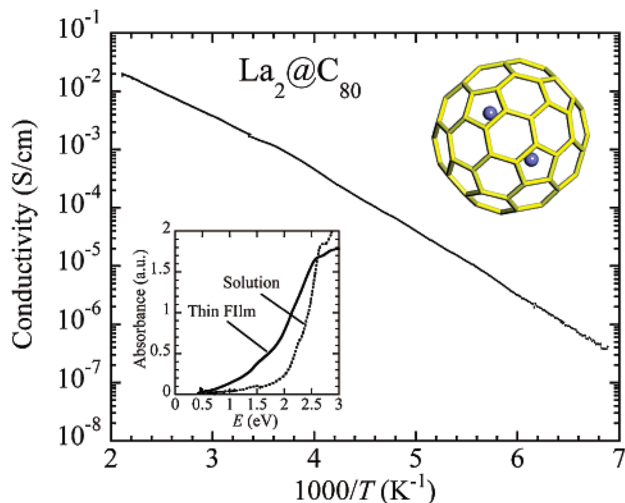

Figure 1. Arrhenius plot of conductivity. Right inset shows a schematic picture of $La_2@C_{80}$ molecule. Left inset displays absorption spectra for thin film and toluene solution of $La_2@C_{80}$.

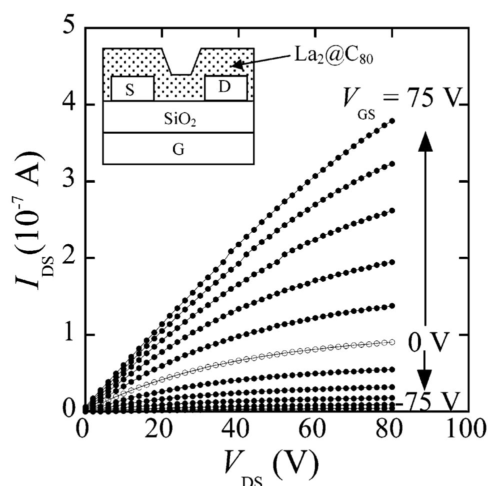

Figure 2. Drain-source current (I_{DS}) is plotted as a function of drain-source voltage (V_{DS}) for several values of gate voltage (V_{GS}). Data sets are displayed for every 15 V from $V_{GS} = -75$ to 75 V. Inset shows a schematic diagram of $La_2@C_{80}$ thin film transistor. S, D, and G denote source, drain, and gate, respectively.

gate-voltage (V_{GS}) values. Relatively large current flow was observed even at $V_{GS} = 0$ V. Application of positive (negative) gate bias increases (reduces) the current I_{DS}. These observations indicate that the electron-type carriers are already unintentionally doped in the nominally undoped material and that the transistor operates in the electron accumulation mode. According to the theoretical[3] and experimental[11] studies on individual $La_2@C_{80}$ molecules, LUMO is dominantly formed of encapsulated La ions. Hence, the present observation of n-type operation of the thin film transistor indicates that the carrier conduction through encapsulated metals is occurring in metallofullerene $La_2@C_{80}$ solids. The origin of carriers that exist without application of the gate voltage remains to be clarified. They may be ascribed to the unintentionally introduced carriers, though the measurement of Figure 2 was made in a very high vacuum in the order of 10^{-9} Torr.

The mobility (μ) and the threshold voltage of the transistor are estimated to be $\mu = 1.1 \times 10^{-4}$ cm^2/V s and -64 V, respectively, from the standard procedure, namely, $(I_{DS})^{1/2}$ vs V_{GS} plot at $V_{DS} =$ 80 V. The low mobility in the order of 10^{-4} cm^2/V s gives a mean-free-path extremely smaller than the molecular size, indicating that the band conduction model suggested from Figure 1 is not correct. A more likely mechanism of carrier transport in the present $La_2@C_{80}$ film would be hopping between grain boundaries or between neighboring molecules.

The mobility of electron carriers in $La_2@C_{80}$ is expected to be intrinsically low, compared to that of C_{60} (ref 12) and C_{70} (ref 13), because of the conduction mechanism through encapsulated metal ions. Since the LUMO is dominated by the orbital of encapsulated La, the intermolecular overlap of LUMOs should be very small, resulting in low mobilities.

The more critical cause of the low mobility is the crystallinity. We have carried out X-ray and electron diffraction experiments and found that the film is poorly crystalline displaying amorphous features. This indicates that intermolecular hopping is a more plausible mechanism of conduction and that the activation energy Δ observed in Figure 1 is regarded as a hopping barrier between neighboring molecules, which are irregularly stacked. On the other hand, the present result implies that the mobility of $La_2@C_{80}$ can be improved by fabrication of films with better crystallinity.

In summary, we have first demonstrated the n-type field effect transistor of dimetallofullerene $La_2@C_{80}$ thin film. Taking the nature of LUMO into account, the n-type behavior of the device indicates an occurrence of carrier conduction through encapsulated La ions. The present experiment revealed the advantage of thin film field effect transistor technique in determining the carrier types and charge transport mechanisms of various endohedral metallofullerenes, which should be more investigated.

Acknowledgment. We thank T. Nishikawa and Seiko EPSON Corporation Technology Platform Research Center M Group for the photolithography technique. This work was in part supported by a Grand-in Aid from MEXT, Japan.

References

(1) For a recent review, see: Shinohara, H. *Rep. Prog. Phys*. **2000**, *63*, 843−892.
(2) Alvarez, M. M.; Gillan, E. G.; Holczer, K.; Kaner, R. B.; Min, K. S.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 10561−10563.
(3) Kobayashi, K.; Nagase, S.; Akasaka, T. *Chem. Phys. Lett*. **1995**, *245*, 230−236.
(4) Nishibori, E.; Takata, M.; Sakata, M.; Taninaka, A.; Shinohara, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2998−2999.
(5) Suzuki, T.; Maruyama, Y.; Kato, T.; Kikuchi, K.; Nakao, Y.; Achiba, Y.; Kobayashi, K.; Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1094−1096.
(6) Fujitsuka, M.; Ito, O.; Kobayashi, K.; Nagase, S.; Yamamoto, K.; Kato, T.; Wakahara, T.; Akasaka, T. *Chem. Lett*. **2000**, 902−903.
(7) Taninaka A.; Shino, K.; Sugai, T.; Heike, S.; Terada, Y.; Hashizume, T.; Shinohara H. *Nano Lett*. **2003**, *3*, 337−341.
(8) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater*. **2002**, *14*, 99−117.
(9) Kazaoui, S.; Ross, R.; Minami, N. *Phys. Rev. B* **1995**, *52*, R11665−R11668.
(10) Kubozono, Y.; Takabayashi, Y.; Shibata, K.; Kanbara, T.; Fujiki, S.; Kashino, S.; Fujiwara, A.; Emura, S. To appear in *Phys. Rev. B*.
(11) Kato, T.; Okubo, S.; Matsuoka, H.; Dinse, K.-P., Proceedings of the International Symposium on Fullerenes, Nanotubes, and Carbon Nanoclusters in 203rd ECS Meeting in Paris 2003, 13; Kamat, P. V., Guldi, D. M., Kadish, K. M., Eds.; The Electrochemical Society, Inc.: Pennington, 2003.
(12) Haddon, R. C.; Perel, A. S.; Morris, R. C.; Palstra, T. T. M.; Hebard, A. F. *Appl. Phys. Lett*. **1995**, *67*, 121−123.
(13) Haddon, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 3041−3042.

JA034944A