Rectification Characteristics of Dual-Layered Organic Device Incorporating Ohmic Contact: Triphenylamine Derivative/C60-Doped Triphenylamine Derivative

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Abstract

In this report, we describe rectification characteristics of a dual-layered organic device sandwitched with Au electrodes. Triphenylamine derivatives are commonly used in organic photoconductors as hole-transport materials for laser-beam printers. In the photoconductors, photogenerated holes are injected easily from a carrier generation layer to the hole-transport layer (HTL). However, in the case of metal/HTL/metal device, it is needed a high voltage for injecting a hole to the HTL even when Au electrode having a large work function is used. For realizing an ohmic contact, we employed a structure of Au/triphenylamine derivative (TPA; the molecular structure is shown in Fig. 1) doped with C60. Then, a metal/TPA/C60-doped TPA/metal was prepared and its rectification property was measured.

Introduction

Various semiconductor device are being mounted on the electronic equipment in which we choose the hand. By using the semiconductor device, the following have been done; Performance enhancement, lightening, miniaturization, power saving of the electronic equipment. These semiconductors are divided into the organic semiconductor which consists of the hydrocarbon with the conjugation π system in which as the rubrene, and inorganic semiconductor which consists of germanium, silicon, etc. At present, the utilization of semiconductor device using the inorganic semiconductor becomes the mainstream because of conduction characteristic being more excellent than the organic semiconductor. On the other hand, the organic semiconductor has the advantage like the following which inorganic semiconductor does not have; (1) Production costs is held it in the energy saving in order to process in low temperature. (2) The area expansion of the device is possible by using the material which is soluble for the solvent. (3) It is possible that it produces the device to which combine the flexibility. From these advantages, the development of the high-performance organic semiconductor is connected for development of electronic equipment and further cost reduction of electronic equipment which there is no ever since.

Previous work on TPA single crystal conductivity.

It is mentioned that the organic single crystal is used for the device in order to realize performance enhancement of organic semiconductor. This is because the transportation of the carrier is easily carried out by the molecular orientation of which single crystal is high. We evaluated the conduction characteristic as single crystal using the triphenylamine derivatives (TPA, Fig.1) of p-type semiconductor used in photoreceptors of laser printer, etc.

We describe anisotropic hole transport in a TPA single crystal prepared by a solution method in other place. Solubility and supersolubility curves were measured employing a tetrahydrofuran (THF) as a solvent (Fig.2). Based on these curves, a single crystal preparation was conducted using a 50 wt.% TPA solution with a suitable cooling rate started from 35°C for 48 h, resulted in a crystal of 6 x 2.5 x 0.8 mm (Fig.3).

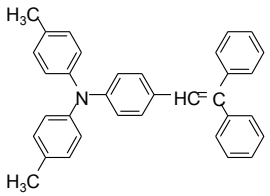


Figure 1. A chemical structure of TPA.

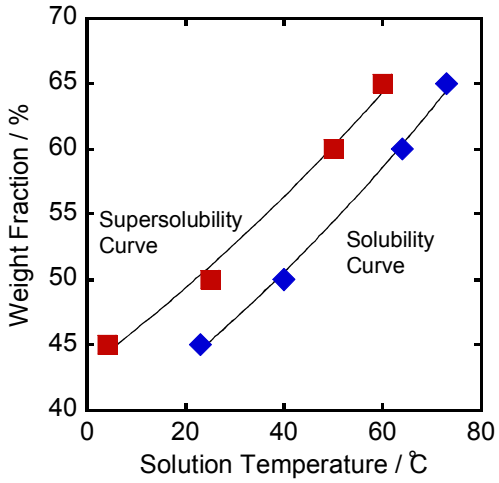


Figure 2. Solubility and supersolubility curves of TPA/THF solution.

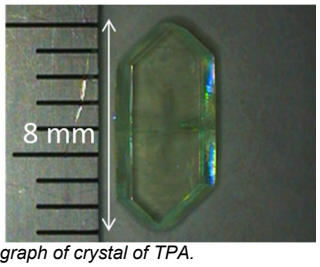


Figure 3. A photograph of crystal of TPA.

From the polarization microscopy and the XRD measurement, it was indicated that obtained crystal was the single crystal.

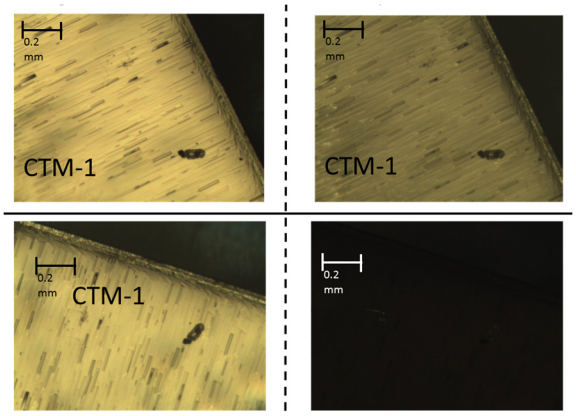
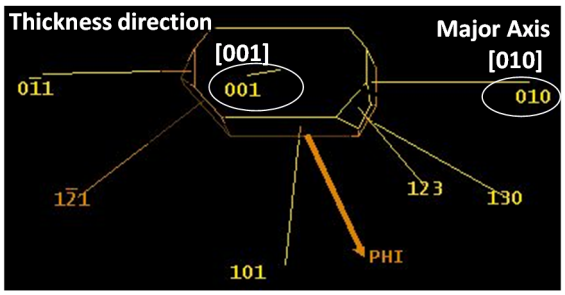


Figure 4. The Reflecting polarization microscopy of ATP crystal.

Figure 4 shows the reflecting polarization microscopy of ATP crystal obtained by above denoted method. The quenching place was able to be confirmed in cross-nicole (tow polarizers were orthogonalized) optical position (right hand side in figure 4), although there is no quenching place in open-nicole (there is a polarizer on the optical path) position (left hand side). It is indicated that the obtained crystal is the single crystal.



$a = 25.102\ (6)$ Å $\quad \alpha = 90.01\ (1)°$
$b = 18.935\ (3)$ Å $\quad \beta = 94.22\ (1)°$
$c = 11.010\ (2)$ Å $\quad \gamma = 90.00\ (2)°$

Figure 5. Lattice constants obtained by the single crystal XRD measurement.

From the single crystal XRD measurement, he lattice constant shown in the figure 5 was obtained. These values were identical with the previous report of which the single crystal of ATP was reported[1]. So we concluded that obtained crystal was the single crystal

Current-voltage properties of the TPA single crystal were measured in a vacuum chamber connected to a source meter. Au parallel electrodes with a distance of 20 μm were vacuum deposited on the crystal. A symmetrical current-voltage characteristic points out that the Au electrodes are equally contacted to the crystal. The major-axis current is larger than the minor-axis current, which reveals anisotropic charge transports in the crystal (Fig.6). This can be well explained by a molecular orientation of the crystal structure.

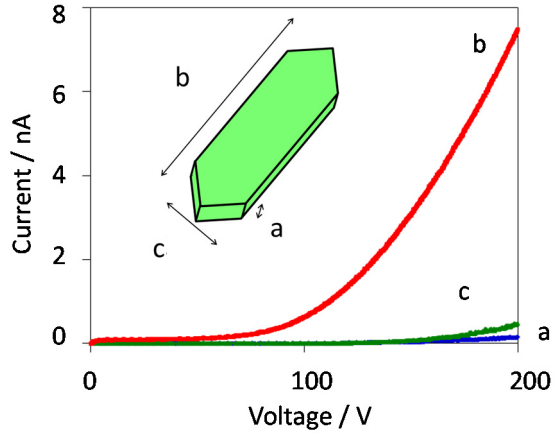


Figure 6. Current-Voltage characteristics in a-axis, b-axis, and c-axis directions of the obtained TPA single crystal.

However, carrier injection barrier called the Schottky barrier exists between TPA and gold (Au) electrode. By this barrier, to some extent large voltage is required so that the device may be made to function from the reason of inhibiting the injection of the hole from Au to the TPA. Therefore, the reduction in the Schottky barrier is very important, and it can be called that it connects it with the drive under low voltage of semiconductor device, in short the power saving in the device use.

Reduction method of the injection barrier.

TPA is p-type organic semiconductor with the hole transport characteristic, and it has been used as hole transport layer of the layered photoelectric conversion device practically. As shown in figure 7, the energy level of the Highest Occupied Molecular Orbital (HOMO) in TPA is about 5.5 eV. Then, work functions of Au is about 5.1 eV. The energy difference of 0.4 eV exists between HOMO of TPA and work function of Au. This energy difference does not work as the barrier, in the case for hole transport is done from HOMO of TPA to the Au electrode. On the other, in the case that hole carriers are injected from Au electrode to TPA HOMO level, this energy difference becomes barrier.

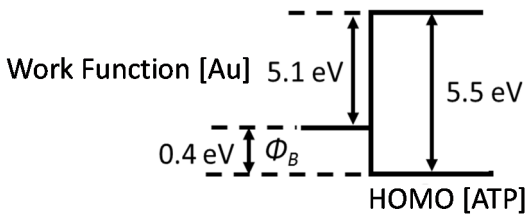


Figure 7. The energy diagram of interface between Au and the ATP.

The method of introducing the fullerene (C60) layer between organic semiconductor and Au electrode is reported as the method in which this carrier injection barrier is reduced [2, 3]. Then, the purpose of this work is that the effect of doping of C60 in TPA on the carrier injection properties are investigated.

Experiments

The layered device was prepared as follows. An Au layer was vacuum deposited on a glass substrate about 20 nm thick. Toluene solutions containing 10wt.% of TPA with C60 (with various molecular ratios) were used to form a C60-doped TPA of 300 nm thick on the Au electrode by a spin-coating technique. Then, a 50 wt.% TPA-tetrahydrofuran (THF) solution was recasted on the C60-doped TPA to make a 2500 nm-thick TPA layer. On the TPA film, a counter Au electrode was vacuum-deposited in the same manner. Thus, the dual-layered organic devices were fabricated as schematically shown in Fig.8.

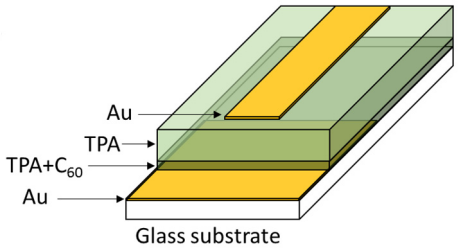


Figure 8. Schematic structure of dual-layered organic device.

Current-voltage properties of the devices were measured in a vacuum chamber connected to a source meter (Keythley 2612A).

Results and Discussion

Figure 9 shows relationships between the applied electric field and the current density as a function of C60-doped amount. As for the without C60-depoed TPA, a symmetrical i-E characteristic is observed, which points out that the Au electrodes are equally contacted to the organic layer. The Richardson-Shottkey plot analysis assessed that the energy barrier for the hole injection is 0.43 eV (detailes are denoted in next sentence). When the C60 is doped in the TPA, the onset electric field shifts toward for getting smaller under the positive electric field; whereas, it does not change under the negative one from Fig. 9. According to an increase in the amount

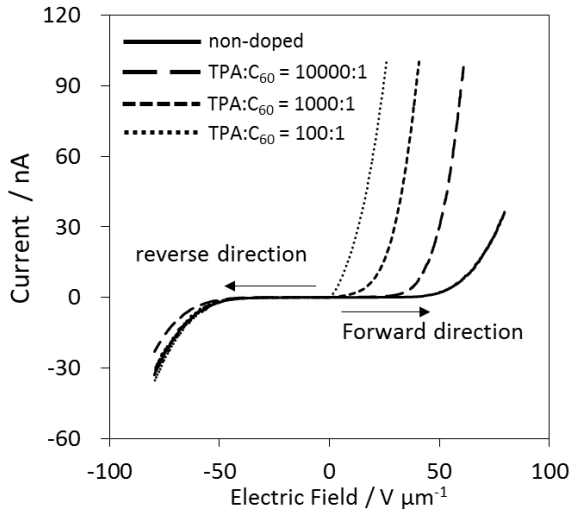


Figure 9. Relationships between the applied electric field and the current density as a function of C60-doped amount.

of doped C60, the onset electric field decreases under the positive field.

Here, the example as the C60-doped TPA sample with a moler ratio of TPA:C60 = 100:2 is taken up, and the calculation of hole injection barrier of a C60-doped TPA film is described. From the J-V characteristic, the Schottky plotting was re-produced as shown in figure 10. From this figure, saturation current density J(0) at each temperature was estimated by extrapolating the linear region at field intensity (these J(0) values are also denoted as a numeral in this figure). It is possible to calculate the value of hole injection barrier by obtaining the gradient by making the Richardson plotting from value of J(0) and its measurement temperature (Fig.11).

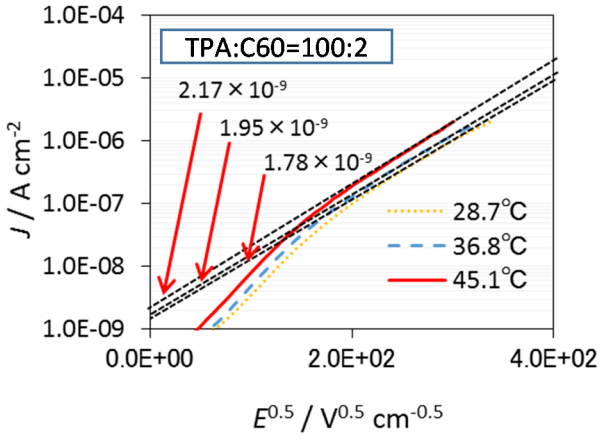


Figure 10. The Schottky plot of the C60-doped TPA layered device with various measurement temperature..

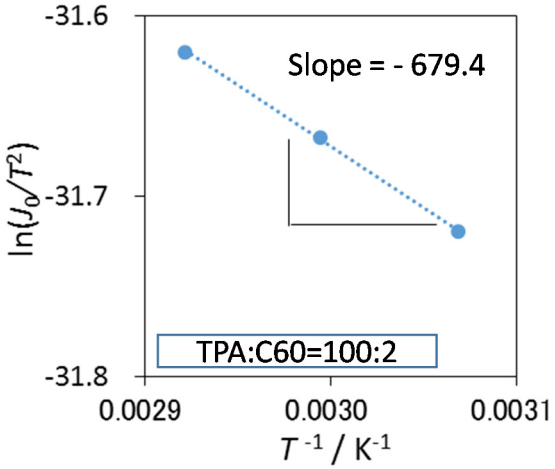


Figure 11. The Richardson plot of the C60-doped TPA layered device.

The dependence of the barrier calculated by doing like this on C60-doping quantity, is shown in figure 12. This result shows that the rapid reduction of the barrier is happening from 0.2 mol% to 0.5 mol% at C60-doping quantity. Therefore, the possibility in which the mechanism of the barrier reduction differed in C60 light dope region (bellow 0.2 mol%) and heavy dope region (over 1.0 mol%)

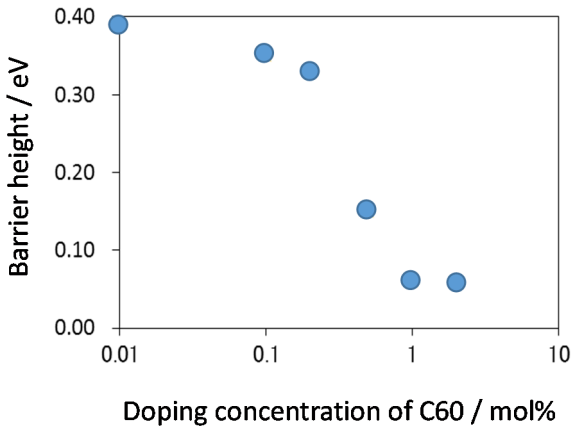


Figure 12. The dependence of the barrier height of Au electrode / C60-doped TPA film interface on C60-doping quantity

was indicated. And, it was proven that the change of barrier height was very small, even if the C60-doping concentration increases in the heavy dope region. From this result, it is indicated to occur from the two factors which differ for the barrier reduction.

Conclusions

By introducing C60-doped TPA layer in the interface of TPA and Au, the reduction in the hole injection barrier was achieved. As this result, it was guessed that the barrier reduction had been produced by the two factors which differ in C60 light dope region and heavy dope region. It is considered that this result is greatly useful, when the mechanism of the barrier reduction will be clarified in future.

The mechanism in which the barrier reduction will happen in future is clarified. This examination can expect the reduction in the carrier injection barrier of various organic semiconductor. And, not only combination of TPA and C60 but also that it generalizes it for all organic semiconductors are required in order to reduce the carrier injection barrier of various organic semiconductor. Therefore, the combination of various organic semiconductors and dope materials will be carried out in the next work.

References

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Author Biography

Norio Nagayama received his B. Eng. and M. Eng. degrees in imaging science from Chiba University in 1992 and 1994, and received his D. Eng. degree in process engineering from Osaka University in 2000. He had been an Assistant Professor at Osaka University since 1998. In 2008, he joined RCOH Company Ltd., and is working on development of organic photo-receptor in Xerographic Printer especially in production printing region. Since 2011, he have been a Visiting Professor at Nagaoka University of Technology. He is a member of the Imaging Society of Japan, and he received Research Encouragement Award of the Society of Electrophotography of Japan in 1997 and same Award of the Imaging Society of Japan in 2004 and 2007. And, he is an Fellow of the Imaging Society of Japan. His research interests focus on applications of organic semiconductors.