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Study on the Charge Injection Barrier in Solution-Processed 6,13-bis(triisopropylsilylethynyl) Pentacene Based Schottky Diodes

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We report on the interfacial characteristics between solution-processed 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) and gold electrodes through controlling the device annealing temperature (DAT) in the schottky diodes. The interfacial characteristics were quantitatively investigated by the height of charge injection barrier from the gold electrode into the TIPS-pentacene layer using Fowler-Nordheim theory. The barrier height was found to be monotonically increased with increasing the DAT. This implies that the contact resistance between the metal electrode and the solution-processed organic semiconductor layer can be definitely increased with a process temperature when such interface is applied to the organic electronic devices.

Keywords Annealing; charge injection barrier; schottky diodes; TIPS-pentacene

Introduction

Recently, organic semiconductor materials have attracted great attention for developing electronic devices such as organic light emitting diodes, organic field effect transistors, and organic solar cells. Among the organic semiconductor materials, pentacene is recognized as an exemplary organic semiconductor with the best electrical properties in organic devices, which is usually prepared by vacuum-deposition technique [1]. However, the traditional vacuum-deposition technique has some drawbacks for large-area and flexible electronics. On this account, solution-processing techniques, such as spin-coating, drop-casting, and dip-coating, are suggested as key strategies for realizing such large-area and flexible electronics by providing low-processing temperatures with low manufacture costs [2,3]. Although solution-processed polymeric semiconductor materials such as poly-3-hexylthiophene have been developed, the electrical properties are quite low compared to those of the

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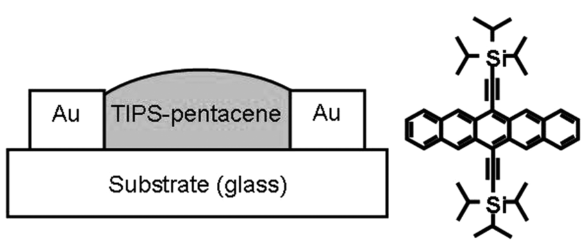
vacuum-deposited materials [4]. Thus, the development of the solution-processable small-molecule is strongly required for enhancing the electrical properties in various types of organic electronic devices. Recently, solution-processed 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) have been introduced by several groups [5,6], which is designed with the addition of two bulky side groups in herringbone crystal structure of pentacene in order to improve the electrical properties in organic electronic devices and solubility in organic solvents [7]. The systematic study of an interface between the TIPS-pentacene and metal electrodes, one of the important interfaces to determine the electrical properties in electronic devices, is considerably needed. Nevertheless, the interface property such as charge injection barrier is not fully understood, so far.

In this work, we have fabricated the solution-processed TIPS-pentacene based schottky diodes which are one of the basic elements in electronic devices and investigated the charge injection barrier as a function of device annealing temperature (DAT) using the Fowler-Nordheim tunneling theory. It was found that the injection barrier heights are monotonically increased with increasing the DAT.

Experimental

Figure 1 shows the schematic diagram of our horizontally fabricated metal-semiconductor-metal (MSM) structure and the chemical structure of TIPS-pentacene. The device is consisted of gold as electrodes and the TIPS-pentacene as a semiconductor for hole-only conduction which is denoted here as a schottky diode. The glass substrate was cleaned with acetone, iso-prophyl alcohol, methanol and deionized water in sequence [8]. For preparing the two electrodes, gold (TAE WON SCIENTIFIC Co., Ltd., 99.99%) was thermally deposited on a glass substrate at a deposition rate of 0.1 nm/s using a typical shadow mask. The thickness of two electrodes is equally to 80 nm. For a solution-processed organic semiconductor, the TIPS-pentacene, dissolved in 1,2-dicholorobenzene in 1.0 wt.%, was drop-casted on the top of the glass substrate and between the gold electrodes. Subsequently, the TIPS-pentacene film was baked at 60°C to remove the solvent. The length and width between two electrodes are 50 mm and 2 mm, respectively. The fabricated TIPS-pentacene based schottky diodes were thermally annealed at different temperatures of 60°C and 150°C. The current density-voltage characteristics were measured using a semiconductor parameter analyzer (HP4155A) under ambient pressure.



(a) (b)

Figure 1. (a) Schematic diagram of a TIPS-pentacene based schottky diode and (b) the chemical structure of a solution-processed organic semiconductor, TIPS-pentacene.

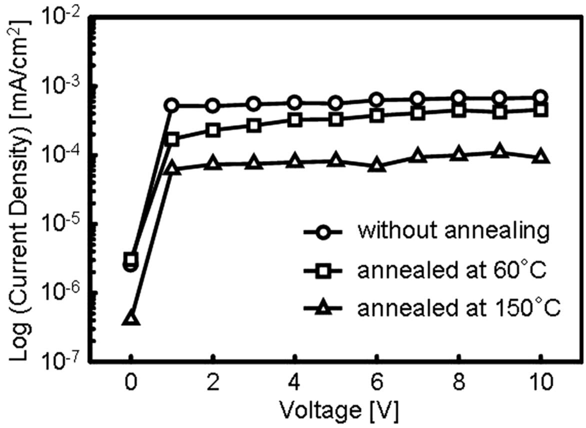


Figure 2. The current density-voltage characteristics of the fabricated hole-only conduction schottky diodes according to the device annealing temperature.

Results and Discussion

Figure 2 shows the current density-voltage characteristics of our schottky diodes with varying the DAT. At an applied voltage of 2 V, the current densities for the devices with non-annealed, annealed at 60°C, and annealed at 150°C, are 5.14×10^{-4}, 2.30×10^{-4}, and $7.32 \times 10^{-5}\,\mathrm{mA/cm^2}$, respectively. It means that the electrical characteristics are significantly deteriorated by the DAT processes. The electrical conductivity in each device is theoretically given by the equation of

$$\sigma = \frac{D}{R \times A}, \tag{1}$$

where R, D, and A are the resistance, thickness of organic semiconductor, and the effective area [9]. The normalized conductivities ($\sigma_{temperature}/\sigma_{no\ annealing}$) of the post-annealed devices to the non-annealed device are summarized in Table 1. As increasing the DAT, the normalized conductivity is decreased from 1 to 0.12. It directly implies that the interface between the gold electrodes and TIPS-pentacene is degraded by the DAT process.

Assuming that the injected hole is tunneling through a triangular barrier at the interface, the height of hole injection barrier can be predicted using Fower-Nordheim tunneling theory,

Table 1. Normalized electrical conductivities in hole-only conducted schottky diodes with varying the device annealing temperature

Temperature	$\frac{\sigma_{temperature}}{\sigma_{no\ annealing}}$
non-annealed	1.00
60°C	0.32
150°C	0.12

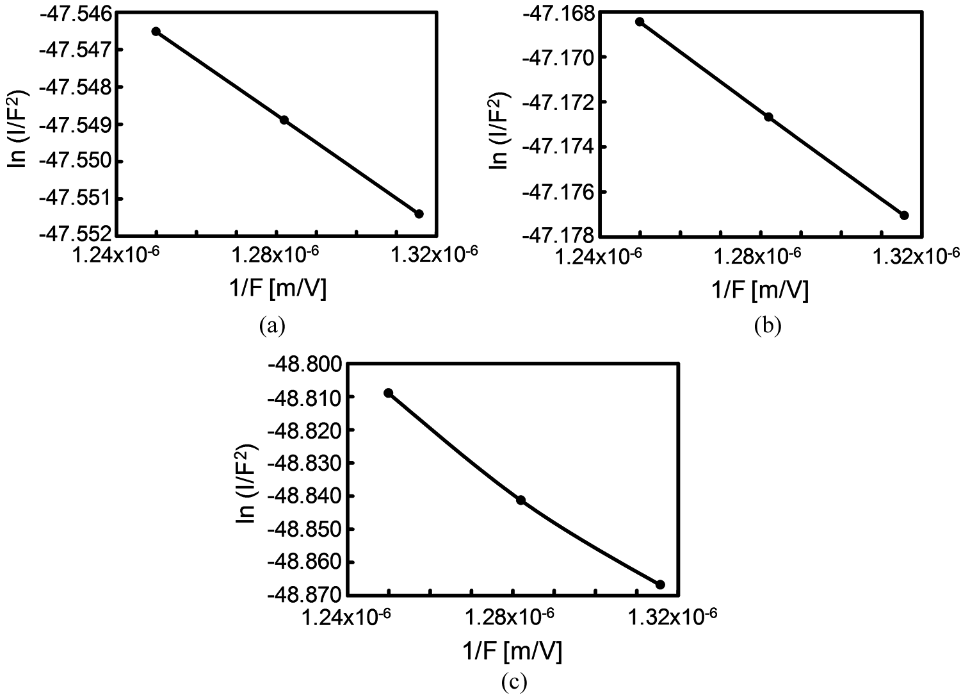


Figure 3. Fowler-Nordheim plots for our TIPS-pentacene based schottky diodes. (a) no-annealed, (b) annealed at 60°C, and (c) annealed at 150°C.

$$I \propto F^2 \exp\left(\frac{-\kappa}{F}\right) \tag{2}$$

$$\kappa = \frac{8\pi\sqrt{2m^*}\Phi^{\frac{3}{2}}}{3qh} \tag{3}$$

where I and F are the current and the electric-field strength, respectively [10,11]. Here, κ is a parameter that depends on the barrier shape, m^* is the effective mass of holes, and Φ is the height of hole injection barrier, respectively. Figure 3 shows the plot of $\ln(I/F^2)$ vs $1/F$ for our schottky diodes. As predicted from the Fowler-Nordheim equation, the plot is almost linear. The normalized barrier heights ($\Phi_{temperature}/\Phi_{no\ annealing}$) of the post-annealed diodes to the non-annealed device case are summarized in Table 2. The normalized barrier height is increased from 1 to 5.19

Table 2. Normalized charge injection barrier heights in schottky diodes with varying the device annealing temperature

Temperature	$\frac{\Phi_{temperature}}{\Phi_{no\ annealing}}$
non-annealed	1.00
60°C	1.45
150°C	5.19

with increasing the DAT. This result theoretically implies that carrier charges (holes in this case) can have the difficulty to be injected into the TIPS-pentacene layer from the gold electrode, induced by the DAT process. Therefore, the degradation in the electrical conductivity, shown in both Table 1 and Figure 2, can be attributed to an increase in the injection barrier height with increasing the DAT. Note that the injection barrier is directly proportional to the contact resistance. It is thought that the contact resistance in TIPS-pentacene based electronic devices will be increased with increasing the post processing temperatures, thereby degrading device performances.

Actually, the contact matter such as contact resistance is one of the critical issues for the electrical properties in electronic devices. Intensive studies have reported that the carrier mobility, which is an important factor dictating the electrical performances of the organic field effect transistors, would be improved by the reducing the contact resistance. For example, the reduction of contact resistance was achieved by using buffer layers and/or surface treatments at the interface between the organic semiconductor and metal electrodes, resulting in enhancements of mobility in thin-film transistors [12,13]. Very recently, as a simple and new approach, an organo-metal hybrid interlayer formed between the organic semiconductor film and metal electrodes using the same materials is also reported [14]. However, most of previous works on reducing the contact resistance are limited within the devices having thermally vacuum-deposited organic semiconductors. Thus, the study on the contact resistance in the solution-processed organic semiconductor is very important for various types of printed electronic devices where the solution-processes are inevitably required.

Let us discuss the contact resistance behavior as a function of the DAT in solution-processed TIPS-pentacene based devices by comparing with that for the vacuum-deposited pentacene based devices. For devices based on the vacuum-deposited pentacene layer, it is reported that the contact resistance is decreased with increasing the DAT [15]. On the other hand, the dependence of the contact resistance on the DAT in our result is diametrically opposed to such previous work. This is presumably resulted from the different growth nature of TIPS-pentacene into films owing to the functional side groups, in contrast to the case of vacuum-deposited pentacene films. Further studies on various organic semiconductors combining with other metal electrodes remain to be carried.

Conclusion

We have studied the interfacial characteristics between solution-processed TIPS-pentacene and gold electrodes with varying the DAT in the schottky diodes. It is found that the hole injection barrier from gold electrode into the solution-processed TIPS-pentacene layer is monotonically increased with increasing the DAT. This results in decreasing the electrical conductivity in the TIPS-pentacene based schottky diode. From our experimental results, we can give the information for the electrical characteristics at the interface in organic electronic devices having the solution-processed organic semiconductor.

Acknowledgments

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