Wet-processed Thin-film Transistors of Pantacene

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Abstract

We have fabricated wet-processed thin-film transistors of unsubstituted pentacene by two kinds of fabrications both solution and dispersion processes. Transistor performances with thin film structures including grain structures in the films by two processes are studied.

1. Introduction

Among the organic semiconductor transistors, pentacene, a small-molecule organic semiconductor is often studied because of its large carrier mobility and on/off ratio. Due to the poor solubility of pentacene in common organic solvents, most of the studies are performed using vacuum deposited films. The performance of the films strongly depends on the film structure, such as grain-size and texture. Solution processing is a promising method for low-cost fabrication of thin films for large area electronics. There have been several reports on solution processing by precursors 1) and substituted pentacene 2).

We have reported a different approach to solution processing of thin films using the solutions of unsubstituted pentacene at elevated temperatures 3). The solution-processed thin-film transistors exhibit large carrier mobility and the films are assumed to be polycrystalline with single crystal domains, though the grain boundaries are not clearly identified.

Recently, we have applied a second approach to forming thin films of pentacene by transferring pre-grown crystals using a liquid process. This dispersion process produces single or poly-crystalline thin films with distinct particulate grains. In order to study the effect of grain boundary on the transport properties, several kinds of dispersion-processed films are fabricated by changing the crystal size and are compared with the films by the solution process.

2. Experimental procedure

By the solution process, the solution is prepared in a glove box under N_2 atmosphere with O_2 content below 5ppm by heating the mixture of pentacene and 1,2,4-trichlorobenzene at 200 ℃. The solution-processed films are fabricated by casting the hot solution on silicon substrate at 190℃ under N_2 atmosphere as previously reported 3). Transistors are fabricated by forming the films on SiO2/Si substrates with patterned Au as source and drain electrodes.

Dispersion-processed films of pentacene are fabricated as follows. Several kinds of crystals with sizes ranging from sub-micron to 50 microns of pentacene are grown in liquid phase from the solution by changing the preparation conditions. Large sized crystals are prepared by slowly cooled the pentacene solution as previously used in the solution-process. Crystal size can be controlled by the cooling rate of the solution since rapid cooling induces fine crystals. Submicron sized crystals are formed by mixing the solution and a poor solvent such as alcohol or acetone. After the growth of particulate crystals, crystals are concentrated by decantation or evaporation of the mixture and are diluted with a dispersion media of isopropanol to form ink. Thin films are prepared by drop-casting the ink on the substrate and vaporizing the dispersion media at room temperature under a nitrogen atmosphere. In some cases, the films are formed under ambient air. Transistors are fabricated by forming the films on SiO2/Si substrates with patterned Au as source and drain electrodes, with the structure of bottom gate and bottom contact.

Measurements on transistor performance of the films are made under vacuum with the pressure below 10^{-2}Pa with a plover (Nagase Grail-43) and a semiconductor parameter analyzer (Keithley 4200). Temperature dependence of transistor performance is measured between –20℃ to 150℃ by controlling the temperature of the substrate holder of the plover. The contact resistance of the films to source and drain electrodes is evaluated by measuring the resistance in a liner regime by applying -5V both drain and gete voltages and changing the channel length from 5 micron to 50 micron.

Film morphologies are measured by scanning electron microscopy, optical microscopy. Out-of-plane and in-plane molecular orientation and crystal structure is measured by wide angle X-ray diffraction pattern and grazing incidence X-ray diffraction patterns, respectively.

3. Results and discussion

The dispersion-processed films are fabricated by coating the dispersion of pentacene crystals in an organic solvent where the crystals are kept in solid state in the dispersion, and then the liquid media is vaporized to form the films. This fabrication process is unique since it is a "built-in system" in contrast to the "build-up system" of conventional thin films both sublimation and solution process.

Thin films are formed with assembled platelet crystals and most of which are aligned with plane facing the substrate surface, confirmed by optical and electron microscopy shown in Figure 1. Crystals of the dispersion-processed films are assumed to aggregate strongly on the substrate since the plate shaped crystals, kept the assembled crystal shape on the transistor channel during the measurements. Some pictures of cross-sectional view show that the crystals are assumed to be soft and bendable.

Molecular orientation of the films is confirmed by measuring the out-of-plane X-ray diffraction pattern, which shows that the pentacene molecules are oriented regularly in the films with long molecular axis perpendicular to the substrate plane, shown in Figure 2. The spacing of the pattern indicates that bulk-phase crystals are formed in the films, which is same with that of solution-processed films. In-plane X-ray diffraction pattern of the dispersion-processed films shows no peaks which indicates that a-axis or b-axis of the pentacene crystal is randomly oriented in the films.

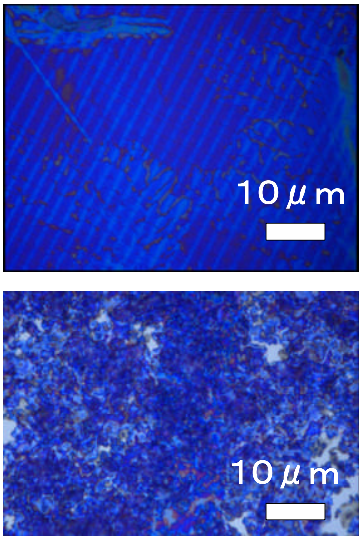

Fig.1. Optical Micrographs of thin films of pentacene, dispersion-processed (lower), and solution-processed (upper)

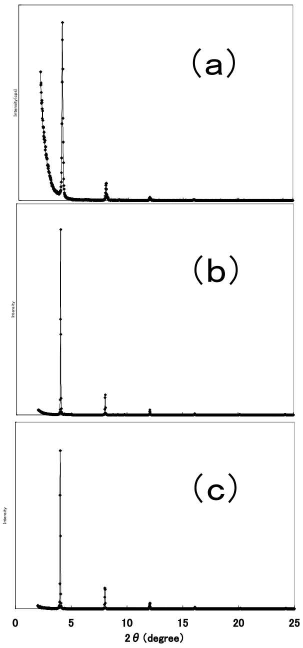

Fig. 2. X-ray diffraction patterns of dispersion-processed films, with average diameter of 0.3μm(a), 2μm(b), and 10μm(c)

Transistors are fabricated by forming the films on SiO2/Si substrates with patterned Au as source and drain electrodes. Single domain thin films assembled with large crystal grain sizes exceeding the channel length exhibit an average carrier mobility of 1cm^2/Vs, which is comparable to the solution processed thin films and single crystals.

Transistors of assembled small crystals with diameter less than the channel length performed well. The carrier mobility of the transistor deceases with the decreasing the crystal size, thus a narrower distribution of the carrier mobility and threshold voltage are observed as shown in Figure 3. It is assumed that the defects such as grain boundaries and vacancies in the films are uniformly distributed. However, expected grain-size-dependent parameters such as the shift of threshold voltage and the on/off ratio of the films are not observed clearly in the dispersion-processed films.

The effect of grain boundaries is studied by both the channel length and temperature dependence on the carrier mobility with changing the crystal size.

The carrier mobility slightly increases of with decreasing channel length in films with small crystals and is independent on channel length with large crystals. This indicates that effect of grain boundaries is less with large crystals, and that the electrode contact resistance is small, which is confirmed by the gradual transfer line method at low applied voltage region. The transport barrier between grain boundaries of the films is determined from the activation-type temperature dependence of the carrier mobility. Temperature dependence of carrier mobility of the dispersion-processed films is presented in Figure 4. It turns out that the transport barrier is ranging from 100 meV of the films assembled with smallest grains to zero of the films with large grains above few microns, which is considerably small compared to the conventional organic thin films of conducting polymers and is comparable to the sublimed thin films of pentacene. The dispersion-processed films formed with large crystals, in which the channel covered with single crystal, show the non-activation temperature

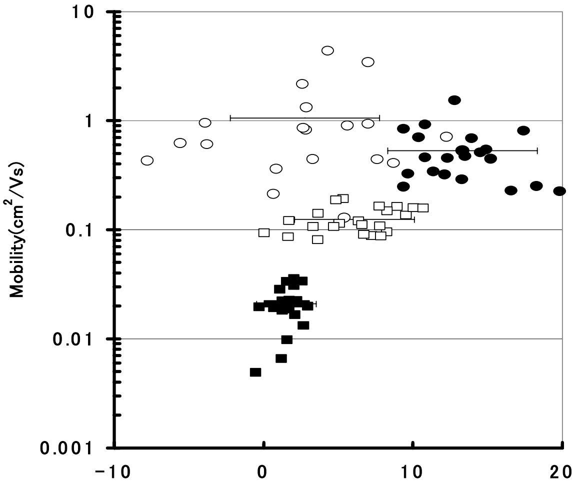

Fig. 3. Mapping of carrier mobility and Vth of dispersion-processed films, with average diameter of 0.3μm(solid square), 2μm (open square), 10μm(solid circle), and 50μm(open circle)

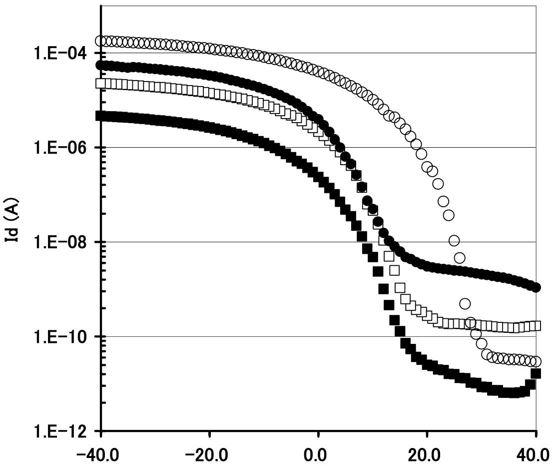

Fig. 4. Typical transfer characteristics of dispersion-processed films, with average diameter of 0.3μm(solid square), 2μm (open square), 10μm(solid circle), and 50μm(open circle)

dependence. This indicates that the carrier transport of the films with large grains is governed by band-like transport. From the results, in dispersion-processed films, the interfacial properties including both the contact resistance of semiconductor crystals to the electrodes and the transport barrier height are found to be small. A plausible explanation for the good contacts between crystals and crystal-electrodes is that the crystals form large contact planes with a smooth surface.

In contrast, the solution-processed film transistors with the average carrier mobility around 1cm^2/Vs show almost temperature independent behavior shown in Figure 5. This indicates that the transport barrier height in the solution-processed is negligible and nice transport path is formed in poly-crystalline films. In comparison with the dispersion-processed films, the assumed crystal size in the solution-processed films is larger then several microns when the same grain-structure model can be applicable. In order to define the difference of texture structures between the dispersion-processed and the solution-processed films, several studies such as the storage performance and the degradation structure are in progress.

4. Summary

A new fabrication process of pentacene thin films by wet-process is indicated. Effects of grain boundaries between crystals are studied by changing film structures with crystal size.

5. References

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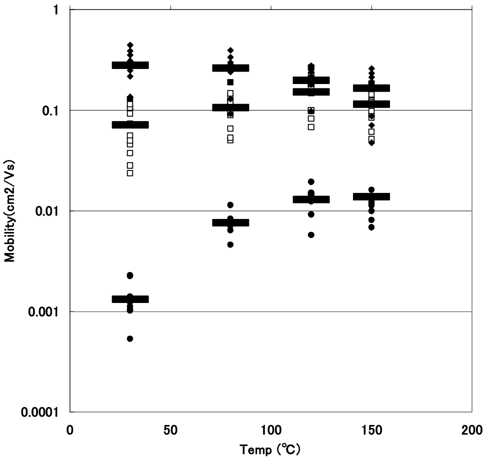

Fig. 5. Temperature dependence of carrier mobility of dispersion-processed films.

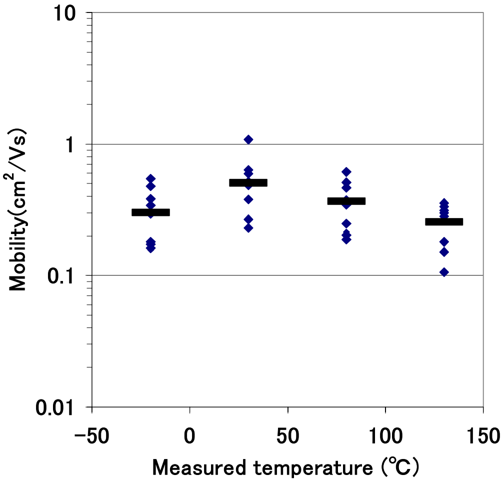

Fig. 5. Temperature dependence of carrier mobility of solution-processed films.