Fabrication of Organic Thin-Film Transistor Using Soluble Dibenzochrysene

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Dibenzo[g,p]chrysene (DBC), which belongs to a cyclic aromatic hydrocarbon similar to pentacene, is drawn attention to. DBC is soluble and dissolves in THF, etc. We estimate the crystal structure of DBC by XRD and the morphology of evaporated and spin-coated DBC thin film by atomic force microscope. DBC is used as the active layer of organic thin-film transistor (TFT). The TFT characteristics cannot be obtained in a top contact-type TFT structure, but those can be done in a bottom contact-type TFT structure using SiO₂/Si substrate. Unfortunately, the TFT mobility is 10⁻⁵ cm²/Vs-order and poorer than that of pentacene TFT because of broken carrier paths between DBC grains and many discrete valleys.

Keywords : dibenzochrysene, organic thin-film transistor, solubility, mobility, FET

1. Introduction

Organic thin-film transistors (OTFTs) can be fabricated at low temperature. That is, it is easy to fabricate OTFTs on plastic films with low heat-resistance. The development of OTFTs attracts increasing attention from many researchers. Recently we are amazed at the rapidity of advance on OTFT characteristics. The carrier mobilities of OTFT using organic single crystal are reported to be beyond 10 cm²/Vs[1-4]. These values are higher than that of amorphous silicone TFT. One is interested in OTFTs using organic single crystals in the viewpoint of physics. However, organic single crystals are not handled easily because of small size and friability. It is important to develop OTFTs which solve the disadvantages of inorganic TFTs. The advantage that OTFTs can be fabricated by low-temperature (<200 °C) process, i.e. spin-coating and printing, is given as an example. The mobilities of OTFTs using pentacene which have been used as an active layer are reported to be at most 1 cm²/Vs[5-7]. However, it is demonstrated that OTFTs with these mobilities can drive liquid crystal and organic light-emitting diode displays[8-15]. The disadvantages are that pentacene films cannot be fabricated by a solution process because of insolubility, that it takes a long

time to fabricate evaporated pentacene films with large grains because of a very deposition rate, and that pentacene is unstable in air because of a narrow HOMO-LUMO gap. Therefore, many soluble and stable materials are developed and reported: for example, TIPS-pentacene[16,17], Cn-BTBTs[18], thiophene oligomers[19], etc[20-26].

We pay attention to dibenzochrysene (DBC). DBC is a cyclic aromatic hydrocarbon similar to pentacene, but is soluble. In this paper, we fabricate DBC films by evaporation and spin-coating methods and study the morphology and film characteristics of DBC films. In addition, we use DBC as an active layer of OTFT for the first time and measure the TFT characteristics of DBC TFT as compared with pentacene.

2. Experimental

Dibenzo[g,p]chrysene (DBC) and pentacene as a reference was obtained from Kurogane Kasei Co.Ltd. Glass substrates were rinsed by supersonic cleaning of water and organic solvents. After UV-ozone cleaning, Cr/Au was evaporated as a gate electrode on a glass substrate. Polyimide thin film was fabricated by spin-coating and post-annealing. Organic semiconductors were

fabricated by a vacuum-deposition method. DBC thin films were also spin-coated on polyimide insulating layer. Finally, Au was evaporated as source and drain electrodes on an organic semiconductor layer. The length and width of channel between source and drain electrodes were $\sim 50\ \mu\text{m}$ and $\sim 2\ \text{mm}$, respectively. We also used the bottom contact-type, SiO_2/Si substrate purchased from Q-Lights. In this case, the length and width of channel between source and drain electrodes were 30 or 50 μm and $\sim 2\ \text{mm}$, respectively. We measured absorption spectra using a spectrophotometer (U-3000; Hitachi Ltd.), ionization potential (I_p) using photoelectron spectroscopy in air (AC-2; Riken Keiki Co. Ltd.), and surface morphology using an atomic force microscope (VN-8000; Keyence Co.). The single crystal analysis of DBC was carried out using microfocus X-ray generators. VariMax optical systems (Rigaku Co.). The TFT characteristics were measured using a source measurement unit (2400 Source Meter; Keithley Instruments, Inc.) in micro vacuum chamber (MJ-8S, Measure Jig Co.Ltd.).

3. Results and Discussions

3.1. Properties and crystal of DBC

DBC dissolves in THF by $>11\ \text{wt\%}$ ($>0.32\ \text{mol/l}$), in chloroform by 6 wt% (0.17 mol/l), and in acetone by 0.35 wt% (0.01 mol/l).

Fig. 1 The absorbance of evaporated DBC and pentacene thin films (thickness, 100 nm) with DBC chemical structure.

Fig. 1 shows the absorbance of evaporated DBC and pentacene thin films (thickness, 100 nm). DBC does not have the absorption in the wavelength region of 400–900 nm. The threshold of absorption of DBC and pentacene are estimated to be 400 nm and 710 nm, respectively. Therefore, the optical

energy gaps of DBC and pentacene are calculated to be 3.1 eV and 1.8 eV, respectively. The ionization potentials of DBC and pentacene are estimated to be 5.9 eV and 5.0 eV, respectively. From these results, DBC is thought to be chemically more stable than pentacene in air.

Fig. 2 The XRD pattern of DBC single crystal

Fig. 2 shows the XRD pattern of DBC single crystal. The crystal structure of DBC is a monoclinic crystal. The crystal index of DBC crystal is $a=12.16\ \text{\AA}$, $b=7.60\ \text{\AA}$, $c=17.67\ \text{\AA}$, $\alpha=90^\circ$, $\beta=97.43^\circ$, and $\gamma=90^\circ$. Fig. 3 shows the molecular alignment in the DBC crystal. We use the follow after calculating crystal indexes.

Fig. 3 The molecular alignment in the DBC crystal

3.2. Morphology and structures of DBC

Fig. 4 shows the AFM image of pentacene film (60 nm) on polyimide insulating film. The deposition rate is 0.0023 nm/s and the substrate temperature is 80 °C. The grain size is 2–3 μm . On the other hand, Figs. 5a and 5b show the AFM images of DBC-evaporated films on glass immediately after deposition. The deposition rates are 0.2 nm/s (5a) and 0.002 nm/s (5b). The roughness of DBC thin film evaporated by the deposition rate of 0.2 nm/s is smooth. In the DBC

film evaporated by the deposition rate of 0.002 nm/s, grains of 1 μm -width and 2~4 μm -height are observed. These morphologies are not stable.

Fig. 4 The AFM image of pentacene film (60 nm) on polyimide insulating film

Fig. 5 The AFM image of as-depo. DBC-evaporated film (100 nm) on glass: (a) 0.2 nm/s, (b) 0.002 nm/s. Top images are expansions of bottom images.

Figs. 6a and 6b show the AFM images of DBC-evaporated films on glass after 3 days, 0.2 nm/s (6a) and 0.002 nm/s (6b). Both film thicknesses are 100 nm (mass-thickness on a quartz oscillator. The thickness of DBC film evaporated by 0.2 nm/s is just 100 nm.). Many small grains of ~0.2 μm -width and 0.5~1 μm -length are observed in both DBC films. These grains are stable.

However, the holes of >1 μm -diameter and 150 nm-depth are also observed especially in Fig. 6b. The holes penetrate from the surface to glass substrate. The change of film morphology is thought to be due to molecular migration. The as-grown DBC thin films are thought to be amorphous. After molecular migration for some days, the DBC thin films will be polycrystallized.

Fig. 6 The AFM image of DBC- evaporated film (100 nm) on glass after 3 days: (a) 0.2 nm/s, (b) 0.002 nm/s.

Fig. 7 The AFM image of DBC-spin-coated film (100 nm) on glass: (a) as-coated, (b) after anneal.

Fig. 7a and 7b show the AFM images of DBC-spin-coated films on glass immediately after coat and annealing. The spin-coating conditions are THF solution (0.05 mol/l) and 2000 rpm. The thickness is 100 nm under the conditions. The anneal conditions are 100 $^{\circ}\text{C}$ for 3 hours under N_2 flow. The roughness of as-grown DBC-spin-coated film is smooth. On the other hand, although the small grains as well as the evaporated DBC film after 3 days are observed, these small grains form some band-like domains. The annealed DBC film morphology is the aggregation of small grains and includes many discrete valleys. This morphology can be observed in annealed DBC-evaporated thin films. It is thought not to be suitable for TFT.

Figs. 8a and 8b show the XRD patterns of as-grown and annealed DBC-evaporated films and as-coated and annealed DBC-spin-coated films, respectively. Any peak are not observed in XRD patterns of as-grown DBC-evaporated and

-spin-coated films. Therefore, as-grown DBC-evaporated and -spin-coated films are amorphous, although DBC forms large domains similar to pentacene.

Fig. 8 The XRD patterns of DBC films (100 nm) on glass: (a) as-coated, (b) after anneal.

The anneal treatment accelerates the polycrystallization of DBC molecules. The crystallization behavior of DBC-evaporated films is different from that of DBC-spin-coated films after annealing. The peak of (210) is observed in both annealed specimens. The peaks of (002) and (110) are observed in the annealed DBC-evaporated film and the peaks of (-101), (101) and (112) are done in the annealed DBC-spin-coated film.

3.3 TFT characteristics of DBC

Fig. 9 shows the typical output characteristics of pentacene TFT fabricated as a reference. The TFT mobility and on/off ratio of our pentacene TFT are $0.5 \text{ cm}^2/\text{Vs}$ and 10^6 , respectively. These values are popular as compared with the others[5,6]. It is found that there is no problem in our TFT measurement system.

Fig. 10 shows the output characteristics of DBC TFT fabricated by spin-coating method. Drain currents do not flow even if gate voltage increases up to 90 V. We cannot obtain TFT characteristics for DBC-evaporated TFT, too. Fig. 11 shows the

AFM image of DBC film fabricated between drain and source channels. The deep valleys between grains are observed in DBC films. Therefore, we conclude that the carrier paths are broken in DBC thin films. Consequently, carriers can little be transported between two electrodes.

Fig. 9 The output characteristics of top-contact type TFT using evaporated pentacene.

Fig. 10 The output characteristics of top-contact type TFT using spin-coated DBC.

Fig. 11 The AFM image of DBC film in channel. We think that our top-contact-type TFT structure using polyimide insulating layer may be unsatisfied with TFT measurement in a low-current region. We try to use bottom-contact-type TFT structure using

SiO₂ insulating layer (400 nm) and p⁺⁺Si gate electrode/substrate. First, we estimate the TFT characteristics of pentacene-evaporated film. The TFT mobility and on/off ratio of our pentacene TFT are 0.05 cm²/Vs and 10⁵, respectively. These values are poorer than those of top-contact-type TFT. This is thought to be due to hydroxyl group on SiO₂[27,28].

(a) Output characteristics of as-depo. DBC TFT

(b) Output characteristics of annealed DBC TFT

(c) Transfer characteristics of the above DBC TFTs

Fig. 12 The TFT characteristics of as-depo. and annealed DBC TFTs.

Fig. 13 The TFT characteristics of annealed DBC-spin-coated TFTs.

Figs. 12 show the output and transfer characteristics of DBC TFTs using evaporated layer. Although drain currents are very low, TFT characteristics can be measured even in an amorphous DBC film. The TFT mobility and on/off ratio of amorphous DBC TFT are 2×10^{-5} cm²/Vs and $<10^2$, respectively. Anneal treatment slightly improves TFT mobility. The TFT mobility and on/off ratio of annealed DBC TFT are 2.5×10^{-5} cm²/Vs and $<10^2$, respectively. Fig. 13 shows the output characteristics of DBC TFTs using spin-coated layer. The TFT characteristics of as-spin-coated DBC layer cannot be measured but those of annealed spin-coated DBC layer can be done. The TFT mobility and on/off ratio of annealed DBC TFT are 1.5×10^{-5} cm²/Vs and $<10^2$, respectively. We speculate that the low TFT mobility of DBC TFT is caused from AFM images by broken carrier paths in DBC grains. Table 1 shows summary of TFT characteristics in this paper.

Table 1 Summarized TFT characteristics.

A. top contact (Au(G)-PI-organic -Au(S-D))

material		μ_h [cm ² /Vs]	on/off ratio	V_{th} [V]
pentacene	annealed	0.27	10 ⁵	-18

B. bottom contact (Si(G)-SiO₂-Au(S-D)-organic)

material		μ_h [cm ² /Vs]	on/off ratio	V_{th} [V]
pentacene	as-depo	0.05	10 ⁵	-8
DBC (eva.)	as-depo	2×10^{-5}	10 ²	-8
DBC	annealed	2.5×10^{-5}	$<10^2$	-23
DBC	as-coated	-	-	-
(SC)	annealed	1.5×10^{-5}	$<10^2$	-1?

‘-’: undetected

4. Conclusions

We fabricated the top-contact-type TFT structure using polyimide insulating layer and the bottom-contact-type TFT structure using SiO₂ insulating layer and p⁺Si gate electrode/substrate, using pentacene and DBC thin films as an active layer. DBC is soluble and a spin-coated DBC layer can be fabricated. We succeeded the fabrication of DBC TFT. Unfortunately, the TFT mobility was low and $\sim 2 \times 10^{-5}$ cm²/Vs. Because the annealed DBC film morphology was the aggregation of small grains and included many discrete valleys.

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