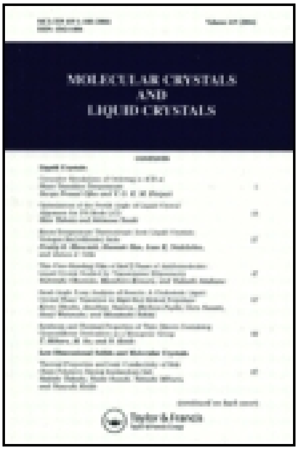

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Fabrication and Field Effect Transistor Characteristics of Well-Ordered Pentacene Film

Hiroki Kihara [a] , Yasukiyo Ueda [a] , Akira Unno [a] & Tadahiko Hirai [a]

[a] Graduate School of Science and Technology, Kobe University, Rokko, Nada, Kobe, Japan

To cite this article: Hiroki Kihara, Yasukiyo Ueda, Akira Unno & Tadahiko Hirai (2004): Fabrication and Field Effect Transistor Characteristics of Well-Ordered Pentacene Film, Molecular Crystals and Liquid Crystals, 424:1, 195-202

To link to this article: http://dx.doi.org/10.1080/15421400490506171

Mol. Cryst. Liq. Cryst., Vol. 424, pp. 195–202, 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490506171

Taylor & Francis
Taylor & Francis Group

FABRICATION AND FIELD EFFECT TRANSISTOR CHARACTERISTICS OF WELL-ORDERED PENTACENE FILM

Hiroki Kihara, Yasukiyo Ueda, Akira Unno, and Tadahiko Hirai
Graduate School of Science and Technology, Kobe University,
Rokko, Nada, Kobe 657-8501, Japan

Pentacene was vapor-deposited on the NaCl substrate and friction-transferred PTFE layer. Pentacene molecules crystallized in bulk phase and/or thin film phase depending on the deposition condition. The polarized absorption spectra of pentacene/PTFE double layer showed an anisotropic feature. Pentacene oriented uniaxially taking edge-on state on a PTFE layer. The electrical property of pentacene/PTFE double layer also indicated anisotropic feature. The field effect mobility along to the traverse of the friction direction was $4.2 \times 10^{-1}\ cm^2/Vs$.

Keywords: FET; friction-transferred PTFE; molecular orientation; polymorph of pentacene

INTRODUCTION

Field effect transistors (FETs) based on organic semiconductors as active layer have received considerable interest. Organic FETs offer several advantages comparing to amorphous silicon transistors like flexibility, low-cost and so on. Pentacene is the most promising material because of its high mobility. It is known that the pentacene forms polymorphs depending on the film thickness [1,2]. These are generally referred to as thin film and bulk phases. Many researchers have investigated the polymorphs of pentacene by means of X-ray diffraction analysis [3,4]. When pentacene films are applied FET, it is very important to prepare high quality and well-ordered films because the electrical properties are related firmly to the

Received 1 October 2003; accepted 10 February 2004.

This work was partially supported by the Photonics Materials Laboratory Project of the VBL of the Graduate School of Science and Technology, Kobe University, and by the Ministry of Education (1355020).

Address correspondence to Hiroki Kihara, Graduate School of Science and Technology, Kobe University, Rokko, Nada, Kobe 657-8501, Japan.

molecular orientation in the film. In general, fabrications of well-ordered organic films have been achieved on certain crystallographic surfaces of metal, ionic and covalent crystals. In such films, bi- or tri-oriented micro grains are frequently caused by the symmetry of the substrate crystals. Recently, high mobility performance of FET has been reported using epitaxially-grown (thiophene/phenylene) co-oligomer film deposited on the alkali halide substrate [5]. From the standpoint of the application to electrical and/or optical devices, preparation of the uniaxially-grown organic films is strongly demanded. Since the pioneering work of Wittmann *et al.* friction-transferred polytetrafluoroethylene (PTFE) layer has attracted a good deal of attention as a substrate to fabricate such films [6].

In this work, pentacene was vapor-deposited on a cleaved surface of NaCl single crystal and friction-transferred PTFE layer. Polymorphism of pentacene was investigated and FET characteristics of the films were also measured.

EXPERIMENTAL

Pentacene was purchased from Tokyo Chemicals Inc. Crude pentacene powder was purified by vacuum-sublimation method. Thin layer of PTFE used as a substrate was prepared on glass supports and heavily doped silicon wafer by the method reported by Wittmann and Smith [6]. The thickness of a PTFE layer was about 10–15 nm. Pentacene was vapor-deposited onto an air-cleaved surface of NaCl single crystal and a friction-transferred PTFE layer kept at various temperatures from a fused silica glass crucible in a vacuum of 10^{-3} Pa. The thickness of the pentacene films was about 50 nm. The structure and absorption characters of the films were investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD) and visible absorption spectroscopy. The electrical measurements were performed in conventional system.

RESULTS AND DISCUSSION

Figure 1 shows absorption spectra of the pentacene films vapor-deposited on a NaCl substrate kept at 80°C with the deposition rate of 0.3 nm/min and kept at 20°C with the deposition rate of 60 nm/min, respectively. Four absorption peaks at 542, 581, 629 and 675 nm are observed in the absorption spectrum of pentacene film prepared by former condition, as shown in Figure 1(a). On the other hand, the absorption spectrum of the film prepared by latter condition shows two absorption peaks at 581 and 667 nm and two shoulders at 542 and 629 nm, as shown in Figure 1(b). XRD pattern of the pentacene film prepared by the corresponding condition with

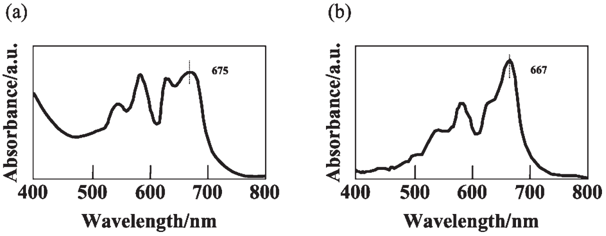

FIGURE 1 Absorption spectra of pentacene films deposited on a NaCl substrate kept at 80°C with the deposition rate of 0.3 nm/min (a) and kept at 20°C with the deposition rate of 60 nm/min (b).

Figure 1(a) shows two peaks corresponding to the interplanar spacings of 1.45 and 0.315 nm, as shown in Figure 2(a). Crystal structure of pentacene has been reported by Campbell [7]. Pentacene crystal is triclinic, space group P$\bar{1}$ with dimensions of a = 0.790 nm, b = 0.606 nm, c = 1.601 nm, $\alpha = 101.9°$, $\beta = 112.6°$ and $\gamma = 85.8°$. On comparison of the observed interplanar spacings and the calculated ones, the peaks in Figure 2(a) coincided with reflections from the (001) and the $(2\bar{1}\bar{1})$ planes, respectively.

On the other hand, XRD pattern of the pentacene film prepared by the corresponding condition with Figure 1(b) shows a single diffraction peak corresponding to the interplanar spacing of 1.54 nm, as shown in Figure 2(b). This peak cannot be accounted by using the unit cell parameters of reported crystal structure and is generally referred as thin film phase. Figures 3(a) and 3(b) show the TEM images and high resolution electron diffraction (HRED) patterns of the pentacene films deposited on a NaCl substrate under the same deposition conditions of Figures 1(a) and 1(b), respectively. HRED patterns were obtained from the area of several tens

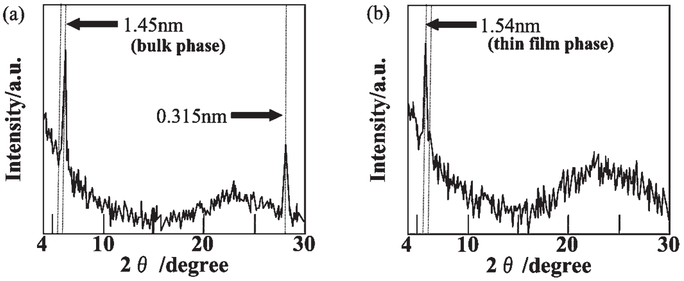

FIGURE 2 XRD patterns of pentacene films deposited on a NaCl substrate kept at 80°C with the deposition rate of 0.3 nm/min (a) and kept at 20°C with the deposition rate of 60 nm/min (b).

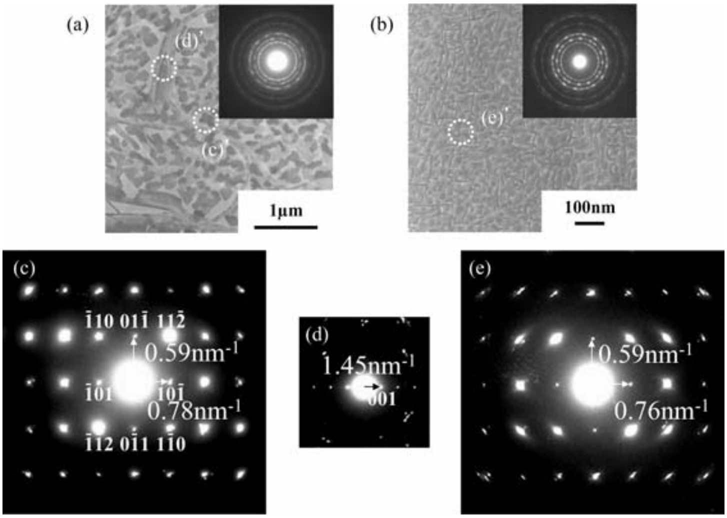

FIGURE 3 TEM images and HRED patterns of pentacene films deposited on a NaCl substrate kept at 80°C with the deposition rate of 0.3 nm/min (a) and kept at 20°C with the deposition rate of 60 nm/min (b). SAED patterns (c), (d) and (e) were obtained from selected area indicated by a circle in (c)', (d)' and (e)' in Figures 3(a) and (b).

micrometer in diameter. The pentacene film consisted of bulk phase was composed of indefinite plate-like crystals with 0.1 μm in size and rod-like crystals with 1 μm in size, as shown in Figure 3(a). The former crystals are predominantly. The HRED pattern of the film showed the ring pattern of the reflection spots corresponding to the interplanar distance of 0.78 and 0.59 nm and those of their higher order reflections. On the other hand, the pentacene film consisted of thin film phase was composed of small crystallites with 10 nm in size, as shown in Figure 3(b). The HRED pattern of the film shows the similar ring pattern. This indicates that the pentacene molecules crystallized in both phases on the NaCl substrate orientate azimuthally. Further structural analysis was carried out for selected area electron diffraction (SAED) patterns of each crystal. Figures 3(c) and 3(d) show the SAED patterns from the selected area indicated by a circle in (c)' and (d)' in Figure 3(a). The SAED pattern in Figure 3(c) showed the single net pattern with the reflection spots corresponding to the interplanar distance of 0.78 nm and 0.59 nm. On comparison of the observed spacings and the calculated ones, the SAED pattern corresponded to the net pattern of $10\bar{1}$ and $01\bar{1}$ reflection spots of the pentacene bulk crystal and their higher order reflections. On the other hand, the diffraction spots on equator of the SAED pattern shown in Figure 3(d) have equidistances corresponding to 001($d = 1.45$ nm) and their higher order reflections of pentacene bulk crystal. The SAED patterns in Figures 3(c) and (d) indicate that the (001) plane and ($2\bar{1}\bar{1}$) plane of bulk crystal oriented parallel to the substrate surface, respectively. Figure 4 represents the molecular orientation of pentacene crystallized in bulk phase on the NaCl substrate. Pentacene molecules in indefinite plate-like crystals adsorbed with the edge-on mode on the substrate surface, as shown in Figure 4(a). On the other hand, the molecular plane of pentacene in rod-like crystals oriented almost parallel to the substrate surface, as shown in Figure 4(b).

The SAED pattern from the selected area indicated by a circle in (e)' in Figure 3(b) showed single net pattern with the reflection spots corresponding to the interplanar distance of 0.76 nm and 0.59 nm, as shown in Figure 3(e). This pattern cannot be indexed using the unit cell parameters of the bulk crystal. It is reasonable to consider that this pattern was obtained from the thin film phase of pentacene crystal because the interplanar distances of those reflection spots are well agreement with those in HRED pattern shown in Figure 3(b). Further information concerning the molecular orientation in the film consisted of thin film phase cannot be obtained at this stage. Figure 5 shows the TEM image and HRED pattern of pentacene film deposited on a friction-transferred PTFE layer kept at 70°C with the deposition rate of 6 nm/min. The pentacene film was composed of plate-like crystals aligned along the sliding direction of the PTFE rod. The HRED pattern of the pentacene/PTFE double layer showed the superposition of the reflection spots from the deposited pentacene crystal and the PTFE layer. The HRED pattern of the pentacene film showed the twined net pattern indicated by arrows with the diffraction spots corresponding to the interplanar distance of 0.76 nm and 0.59 nm. Each net pattern coincided to the pattern obtained from the crystallite of thin film phase shown in Figure 3(e). Ring pattern also appeared. Therefore it seems that the pentacene molecules oriented partially on the PTFE layer. Knipp *et al.* carried out the structure analysis of pentacene thin film deposited on

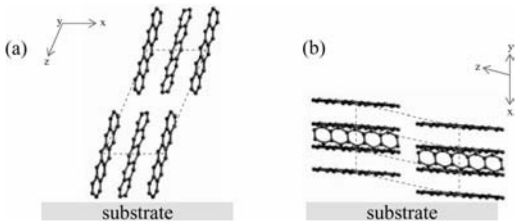

FIGURE 4 Schematic representation of the molecular orientations of pentacene in the indefinite plate-like crystal (a) and rod-like crystal (b).

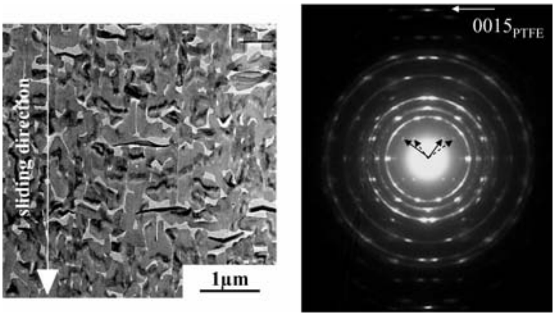

FIGURE 5 TEM image and ED pattern of pentacene film deposited on a friction-transferred PTFE layer kept at 70°C with the deposition rate of 6 nm/min.

a silicon nitride by using X-ray diffraction [8]. They pointed out that thin film phase structure is almost similar to bulk crystal structure except for the tilting angle of pentacene molecules against to the basal plane normal. In bulk crystal, pentacene molecules tilt at an angle of 25.7° against to the (001) plane normal. They speculated that the tilting angle in thin film phase is 17.1° from the shift of reflection peak to low diffraction angle. Therefore, we concluded that pentacene molecules form column structure taking edge-on state on the PTFE layer.

In order to obtain the information concerning molecular orientation in the film, polarized absorption measurement was carried out. Figure 6 shows the polarized absorption spectra of the pentacene/PTFE double layer. The maximum absorption peak of the deposited pentacene appears at 667 nm. This also supports that pentacene film is composed of thin film phase in a whole area of pentacene/PTFE double layer. The transition

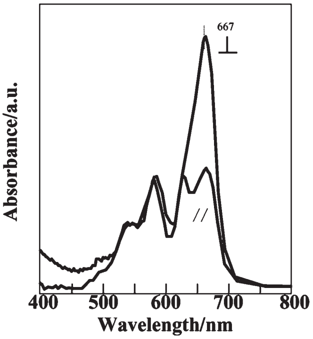

FIGURE 6 Polarized absorption spectra of pentacene/PTFE double layer.

moment of the lowest singlet exciton associated with π-π^* band-gap of pentacene molecule is parallel to the longitudinal direction of the molecule. Because pentacene molecules adsorbed obliquely on the substrate surface taking edge-on state, only the projected component of transition moment of pentacene molecule interacts with the electric field induced by incident light. It is noteworthy that the double layer indicates an anisotropic feature in polarized absorption properties. This indicates that the projected component of transition moment aligned normal to the sliding direction of PTFE rod. Therefore, it is concluded that the column axis in the thin film phase aligned also normal to the sliding direction.

In order to clarify the relation between the molecular orientation and electrical properties, I_{DS} versus V_{DS} measurement of pentacene/PTFE double layer was carried out. PTFE layer friction-transferred on a highly doped silicon wafer was used as a substrate. In this case, highly doped silicon was used not only as a substrate but also as gate electrode, while the thermally grown SiO_2 was used as gate insulator. Au was deposited as source and drain electrodes along to the friction direction and along to the traverse of friction direction. The channel length and width were 90 and 900 μm. When the gate electrode was biased positively, FET operated in the depletion mode. On the other hand, when the gate electrode was biased negatively, it operated in the accumulation mode. Figure 7(a) shows the

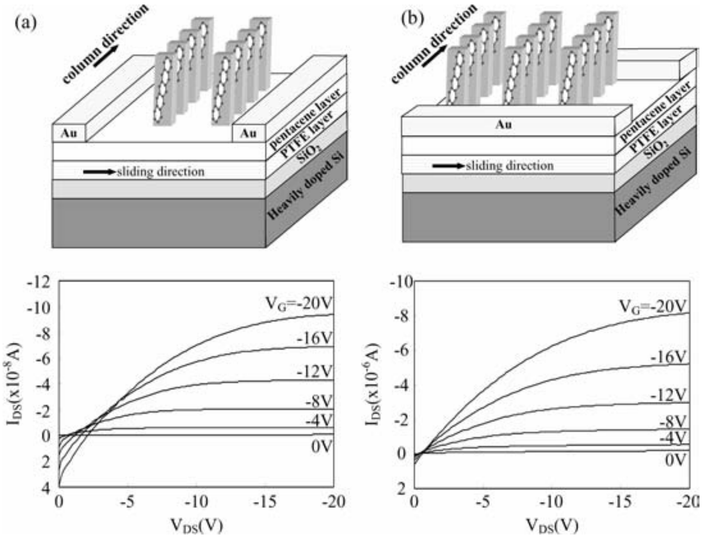

FIGURE 7 I_{DS} versus V_{DS} characteristics along to the friction direction (a) and along to the traverse of the friction direction (b) of pentacene/PTFE double layer. Constructions of FET are also indicated schematically in the figure.

source-drain current (I_{DS}) versus source-drain voltage (V_{DS}) characteristics with various gate voltages (V_G) along to the friction direction of pentacene/PTFE double layer. The FET characteristic was clearly observed. The field effect mobility along to the friction direction was $5.9 \times 10^{-3}\,\mathrm{cm}^2/\mathrm{Vs}$. Figure 7(b) shows I_{DS} versus V_{DS} characteristics with various V_G along to the traverse of friction direction of pentacene/PTFE double layer. Remarkable enhancement is obtained of I_{DS}. The field effect mobility along to the traverse of the friction direction was $4.2 \times 10^{-1}\,\mathrm{cm}^2/\mathrm{Vs}$. Charge-carrier mobility is probably much larger through the molecular columns in the uniaxially-oriented film, which results in a higher I_{DS}.

CONCLUSION

Pentacene was vapor-deposited on the NaCl substrate and friction-transferred PTFE layer. The polymorphism of pentacene in the film was heavily dependent on the deposition condition. When pentacene was vapor-deposited on a NaCl substrate kept at 80°C with the deposition rate of 0.3 nm/min, pentacene molecules crystallized in bulk phase. On the other hand, thin film phase formed in the film deposited on a NaCl substrate kept at 20°C with the deposition rate of 60 nm/min. Pentacene oriented uniaxially taking edge-on state on a PTFE layer. The field effect mobility through the molecular columns was $4.2 \times 10^{-1}\,\mathrm{cm}^2/\mathrm{Vs}$. which was about 100 times larger than that along the traverse of the column.

REFERENCES

[1] Minakata, T., Imai, H., Ozaki, M., & Saco, K. J. (1992). *Appl. Phys., 72*, 5220.

[2] Dimitrakopoulos, C. D., Brown, A. R., & Pomp, A. J. (1996). *Appl. Phys., 80*, 2501.

[3] Gundlach, D. J., Lin, Y. Y., Jackson, T. N., & Schlom, D. G. (1997). *IEEE Electron Device Lett., 18*, 87.

[4] Bouchoms, I. P. M., Schoonveld, W. A., Vrijmoeth, J., & Klapwijk, T. M. (1999). *Synth. Met., 104*, 175.

[5] Ichikawa, M., Yanagi, H., Shimizu, Y., Hotta, S., Koyama, T., & Taniguchi, Y. (2002). *Adv. Mater., 14*, 1272.

[6] Wittmann, J. C. & Smith, P. (1991). *Nature, 352*, 414.

[7] Campbell, R. B., Robertson, J. M., & Trotter, J. (1962). *Acta Cryst., 15*, 289.

[8] Knipp, D., Street, R. A., Krusor, B., Apte, R., & Ho, J. J. (2002). *Non-Crystalline Solids, 299*, 1042.