

# Lattice Defects of Naphtacene Single Crystals Obtained by Physical Vapor Transport Technique Investigated by White-Beam X-ray Topography

Sadaharu JO

Lattice defects of naphtacene single crystals obtained by the physical vapor transport technique were investigated by white-beam X-ray topography, which revealed line patterns along the crystallographic [110] direction as dislocation lines. The estimated dislocation density indicates that the crystals are of superior quality.

**Keywords:** naphtacene single crystal, physical vapor transport technique, white-beam X-ray topography, lattice defect, dislocation

## 1. Introduction

Organic devices have a high potential for sub-nanoscale applications in next-generation flexible electronics.<sup>1-14</sup> The use of the physical vapor transport (PVT) technique to obtain organic single crystals has been increasing<sup>15-29</sup>, and such crystals have been focused on for their applications in various types of device, such as solar cells, field-effect transistors, and light-emitting diodes.<sup>30-35</sup> There are high expectations that the high crystallographic periodicity and ideal electronic structures of these crystals can be retained because most impurities can be excluded during the physical vapor growth process. Naphtacene, a chainlike aromatic molecule composed of four benzene rings, is a promising material for many device applications; however, only a few scientific evaluation studies of naphtacene crystal defects have been performed thus far. X-ray topography is a powerful method of characterizing crystal quality, because various types of dislocation in Laue spots can be observed directly as topographic images. Crystal quality is reduced by the included impurities, strain, the disorder of periodicity, and other factors. For the precise control of electronic characteristics, high-quality single crystals with perfect and ideal periodicity

are required. Thus, it is extremely important to investigate and determine suitable conditions for obtaining high-quality organic single crystals. In this paper, the quality of naphthalene single crystals obtained by the PVT technique (PVT-naphthalene single crystals) is discussed on the basis of the results of a morphological investigation and white-beam X-ray topography.

## 2. Experimental Procedure

The naphthalene single crystals investigated in this study were obtained by the PVT technique. Fig. 1 shows a schematic of our handmade growth furnace, which was composed of a reaction tube, a growth tube, a source boat, a resistance wire, and a band heater. The lengths of the reaction and growth tubes were 500 and 250 mm, and the diameters were 30 and 25 mm, respectively. Tubes of 5 mm diameter were set along both ends of the reaction tube to enable the flow in and out of a carrier gas that circulates evaporated source materials by forced convection. The reaction tube was surrounded by a resistance wire at equal intervals for maintaining the desired temperature in the furnace. A band heater was placed at the same location as the source boat to generate a temperature gradient. To obtain PVT-naphthalene single crystals, the growth temperature was varied between 220 and 400 °C. Helium gas was employed as the carrier gas and its flow rate was fixed at 50 ml · min<sup>-1</sup>. After the crystal growth by the PVT technique, the growth tube including the PVT-naphthalene single crystals was removed from the furnace. The crystal morphology was investigated by several types of optical microscopy technique. For crystallographic characterization based on the Laue method, the white-beam X-ray topography apparatus at SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), BL28B2 beamline was employed. The apparatus was arranged in accordance with the forward reflection Laue method. The available X-rays had a wide energy band with an energy higher than 5 keV. The critical energy of the X-rays was 28.9 keV. To reduce the damage to the crystals caused by X-ray irradiation, a water filter unit of 5 mm path length was attached. The crystal quality was sufficiently high for conducting white-beam X-ray topography more than ten times. The camera length was set at 120 mm. The slit dimensions were set at 5×5 mm<sup>2</sup>, and the X-ray irradiation time was varied from 10 to 30 s. Specimens were set with the plane with the largest width normal to the incident X-ray beams, which is the [001] direction. The normal direction corresponds to the [001] direction. To determine the crystallographic indices, specific programs, namely, the Laue Pattern Digitize & Laue Analysis & Result Display Program and the Laue Pattern & StereoGraphic Projection Display Program, which were originally produced for our study by Norm Engineering Co. Ltd., were employed. Diffractometry was also performed to precisely investigate the quality of PVT-naphthalene single crystals.

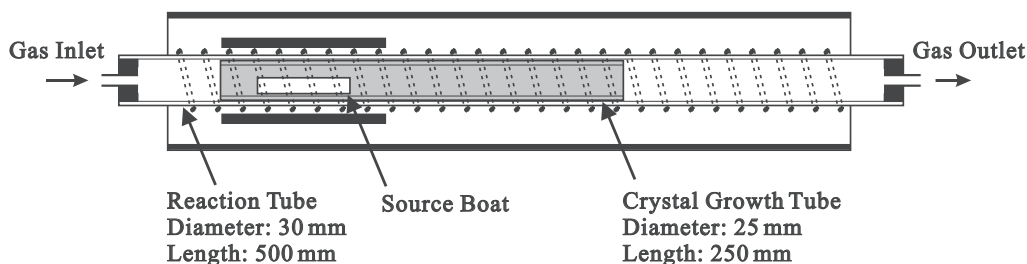


Fig. 1 Schematic of growth furnace for obtaining naphtacene single crystals by PVT technique.

### 3. Results and Discussion

As shown in Fig. 2, the typical morphology of a PVT-naphtacene single crystal is plateletlike with a large-width hexagonal plane, which is surrounded by very thin lateral planes. The width of a plateletlike crystal is ca. 10 mm and the thickness is only ca. 500 nm. Many plateletlike crystals possessed planes with larger widths of 20–30 mm. The crystallographic index of the hexagonal plane with a large width was characterized to be the (001) plane by diffractometry, as described in our previous report<sup>25</sup>. The narrow lateral planes were formed by {100} and {110} planes.

Fig. 3(a) shows a Laue pattern of a PVT-naphtacene single crystal. Many Laue spots with high intensity can be recognized in the pattern. The large black shadow at the bottom of Fig. 3(a) corresponds to the direct-beam stopper of the X-ray apparatus. The spot arrangement perfectly agrees with that of the basal (001) pattern for naphtacene with a triclinic system:  $a=7.90 \text{ \AA}$ ,  $b=6.03 \text{ \AA}$ ,  $c=15.53 \text{ \AA}$ ,  $\alpha=100.3$ ,  $\beta=113.2$ , and  $\gamma=86.3$ <sup>36</sup>. The configuration of Laue spots indicates the crystal morphology and suggests that the crystal we obtained includes little strain and possesses long-range coherent periodic structures, because even the Laue spots with high indices such as 623 and 432 spots indicate that the crystal configuration is still maintained with little elongation. As described in our previous report<sup>25</sup>, large PVT-naphtacene single crystals are of excellent quality; however, the small PVT-naphtacene single crystals are of inferior quality. It appears that the small PVT-naphtacene single crystals cannot grow further because of the inclusion of strain. Figs. 3(b) and (c) show enlarged topographs of the  $\bar{3}\bar{2}\bar{4}$  and  $\bar{2}\bar{3}0$  reflections, respectively, which were recorded with the incident white beam parallel to the

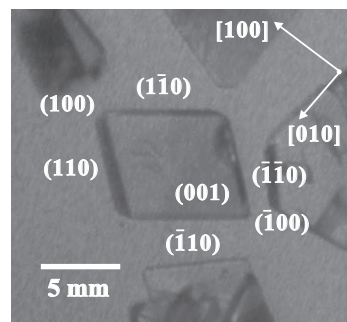
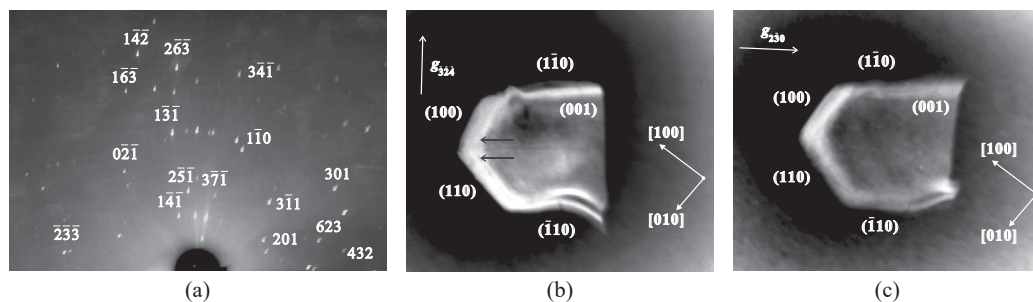


Fig. 2 Typical morphology of naphtacene single crystal obtained by PVT technique.

[001] direction. Both topographs substantially reflect the crystal configuration. As observed in Fig.3 (b), several line patterns with dark contrast are nearly parallel to the [110] direction, which are indicated by two black arrows. This experimental result excellently agrees with the report of Pflaum et al. indicating that the formation of side edges of grooves occurs along the [110] direction<sup>37</sup>; they, however, obtained their naphthalene crystals by the solution technique. On the basis of the theory of the invisible criterion for the dislocation contrast, the dislocations in images are assumed to be invisible at  $\mathbf{g}\cdot\mathbf{b}=0$ . Here,  $\mathbf{g}$  is the diffraction vector and  $\mathbf{b}$  is the Burgers vector. When assuming that the origin of a line pattern is a screw dislocation, line patterns should be invisible or visible with weak contrast in Fig. 3(b); on the other hand, when assuming that the origin of a line pattern is an edge dislocation, line patterns should be invisible or visible with weak contrast in Fig. 3(c). Actually, the line patterns are visible, when they are normal to the diffraction vector of  $\mathbf{g}_{\bar{3}\bar{2}\bar{4}}$ , as seen in Fig. 3(b); however, the line patterns are invisible when they are parallel to the diffraction vector of  $\mathbf{g}_{2\bar{3}0}$ , as seen in Fig. 3(c). Thus, the line patterns seen in Fig. 3(b) are possibly the dislocation lines formed owing to the edge dislocation. The expected orientation of the Burgers vector of the edge dislocation is in the [320] or [001] direction. Thus, this result indicates that crystallographic slip planes form easily along the [320] or [001] direction. Electronic carriers can possibly overcome the energy barrier against the slip planes. Moreover, the dislocation density was estimated to be ca.  $1.0\times 10^3$   $\text{cm}^{-2}$ . Koizumi et al. described that organic crystals with ordered dislocation densities of  $10^2$ – $10^3$   $\text{cm}^{-2}$  are of high quality<sup>38</sup>; hence, we consider that our PVT- naphthalene single crystals investigated in this study are of high quality.



**Fig. 3** (a) Laue pattern of naphthalene single crystal grown by PVT technique. The incident X-ray beam was parallel to the [001] direction. (b) and (c) show enlarged topographs of the  $\bar{3}\bar{2}\bar{4}$  and  $2\bar{3}0$  reflections, respectively.

#### 4. Conclusion

Lattice defects of PVT-naphthalene single crystals were investigated by white-beam X-ray topography.

The dislocation lines observed parallel to the crystallographic [110] direction originated from edge dislocations, as confirmed on the basis of the theory of the invisible criterion for the dislocation contrast. The estimated dislocation density indicates that the crystals are of superior quality.

## Acknowledgements

This research was partially supported by the Nanotechnology Network Japan Program (Nanonet) and Nanotechnology Platform Japan Program (Nanotech Japan), The Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (Proposal Nos. 10–14 (2010TTI), 11–01 (2011TTI), 2012-F12-TT-0006 (2012TTI), and 2014-F14-TT-0014 (2014TTI)). The synchrotron radiation experiments were performed at SPring-8 with the approval of JASRI (Proposal Nos. 2003B0068, 2004A0212, 2005B0363, and 2006B1278; BL28B2). The author would like to thank Professor M. Yoshimura (Toyota Technol. Inst.), Dr. S. Suzuki (JAEA), Dr. M. Ataka (AIST), Professor K. Izumi (Kyoto Univ.), Dr. K. Kajiwara (JASRI), Dr. S. Maki (Okayama Univ. Sci.), Professor T. Kohzuma (Ibaraki Univ.), and Professor M. Takenaga (Tokyo Univ. Sci., Yamaguchi) for cooperation in experiments and fruitful discussions.

## References

- 1 N. Alharbi, J. Hart, and J. N. O'Shea: *Surf. Sci.* **735** (2023) 122323.
- 2 S. J. Konezny, M. N. Bussac, and L. Zupponi: *Phys. Rev. B* **81** (2010) 045313.
- 3 J. C. Bijleveld, R. A. M. Verstrijden, M. M. Wienk, and R. A. J. Janssen: *Appl. Phys. Lett.* **97** (2010) 073304.
- 4 J. Park, H. M. Kim, D. W. Kim, and J. S. Choi: *Appl. Phys. Lett.* **97** (2010) 093301.
- 5 M. Wagner, F. Calcinelli, A. Jeindl, M. Schmid, O. T. Hofmann, and U. Diebold: *Surf. Sci.* **722** (2022) 122065.
- 6 A. Winkler: *Surf. Sci.* **643** (2016) 124.
- 7 B.-N. Park, S. Seo, and P. G. Evans: *J. Phys. D, Appl. Phys.* **40** (2007) 3506.
- 8 A. K. Mukherjee, A. K. Thakur, W. Takashima, and K. Kaneto: *J. Phys. D, Appl. Phys.* **40** (2007) 1789.
- 9 E. Y. Kataev, L. Fromm, Q. Tariq, D. Wechsler, F. J. Williams, N. Tsud, S. Franchi, H.-P. Steinruck, A. Gorling, and O. Lytken: *Surf. Sci.* **720** (2022) 122007.
- 10 A. Venalainen, K. Meinander, M. Raisanen, V. Tuboltsev, and J. Raisanen: *Surf. Sci.* **677** (2018) 68.
- 11 T. Manaka, E. Lim, R. Tamura, and M. Iwamoto: *Thin Solid Films* **499** (2006) 386.
- 12 Z. V. Vardeny, A. J. Heeger, and A. Dodabalapur: *Synth. Met.* **148** (2005) 1.
- 13 J. Brox, B. Adhikari, M. Shaker, M. Ruppel, N. Jux, H. Maebach, S. Jaekal, and H.-P. Steinruck: *Surf. Sci.* **720** (2022) 122047.
- 14 J. G. Park, G. T. Kim, J. H. Park, H. Y. Yu, G. McIntosh, V. Krstic, S. H. Jhang, B. Kim, S. H. Lee, S. W. Lee, M. Burghard, S. Roth, and Y. W. Park: *Thin Solid Films* **393** (2001) 161.
- 15 N. Karl: *J. Cryst. Growth* **99** (1990) 449.

- 16 G. Hollowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J.-L. Fave, and F. Garnier: *Chem. Mater.* **7** (1995) 1337.
- 17 R. A. Laudise, Ch. Kloc, P. G. Simpkins, and T. Siegrist: *J. Cryst. Growth* **187** (1998) 449.
- 18 Ch. Kloc, P. G. Simpkins, T. Siegrist, and R. A. Laudise: *J. Cryst. Growth* **182** (1997) 416.
- 19 S. Jo and M. Takenaga: *J. Phys. Conf. Ser.* **258** (2010) 0120171.
- 20 S. Jo and M. Takenaga: *Jpn. J. Appl. Phys.* **49** (2010) 078002.
- 21 S. Jo, K. Okamoto, and M. Takenaga: *Appl. Surf. Sci.* **256** (2010) 1969.
- 22 S. Jo, N. Takada, and M. Takenaga: *J. Phys. Soc. Jpn.* **82** (2013) 135001.
- 23 S. Jo, K. Kajiwara, and M. Takenaga: *Jpn. J. Appl. Phys.* **53** (2014) 115506.
- 24 S. Jo, S. Suzuki, and M. Yoshimura: *Thin Solid Films* **554** (2014) 154.
- 25 S. Jo, N. Takada, and M. Takenaga: *Jpn. J. Appl. Phys.* **50** (2011) 065501.
- 26 S. Jo, H. Yoshikawa, A. Fujii, and M. Takenaga: *Synth. Met.* **150** (2005) 223.
- 27 N. Yoshimoto, T. Kakudake, K. Aosawa, and Y. Saito: *J. Cryst. Growth* **310** (2008) 1725.
- 28 R.-F. Xiao: *J. Cryst. Growth* **174** (1997) 821.
- 29 F. Pan, Ch. Bosshard, M. S. Wong, C. Serbutoviez, S. Follonier, P. Gunter, and K. Schenk: *J. Cryst. Growth* **165** (1996) 273.
- 30 D. Paoloni and A. Ruocco: *Surf. Sci.* **735** (2023) 122322.
- 31 X. Zeng, D. Zhang, L. Duan, L. Wang, G. Dong, and Y. Qiu: *Appl. Surf. Sci.* **253** (2007) 6047.
- 32 W. E. Carswell, M. I. Zugrav, F. C. Wessling, and G. Haulenbeek: *J. Cryst. Growth* **211** (2000) 428.
- 33 M. D. J.-Sanchez, N. S.-Abad, N. Nicoara, and J. M. G.-Rodriguez: *Surf. Sci.* **710** (2021) 121848.
- 34 J. Knudsen, J. N. Andersen, and J. Schnadt: *Surf. Sci.* **646** (2016) 160.
- 35 K. Gotz, I. Stollberg, A. Prihoda, F. Bertram, E. Metwalli, and T. Unruh: *Surf. Sci.* **721** (2022) 122066.
- 36 J. E. Northrup, M. L. Tiago, and S. G. Louie: *Phys. Rev. B* **66** (2002) 121404.
- 37 J. Pflaum, J. Niemax, and A. K. Tripathi: *Chem. Phys.* **325** (2006) 152.
- 38 H. Koizumi, M. Tachibana, K. Kojima, and I. Yoshizaki: *Space Utiliz. Res.* **21** (2005) 98.