

Bulk-like pentacene epitaxial films on hydrogen-terminated Si(111)

Toshihiro Shimada, Hiroyuki Nogawa, Tetsuya Hasegawa,
Ryusuke Okada, and Hisashi Ichikawa

Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

Keiji Ueno

Department of Chemistry, Saitama University, Sakura-ku, Saitama, 338-8570 Japan

Koichiro Saiki

Department of Chemistry and Department of Complexity Science and Engineering, The University of Tokyo, Kashiwa, Chiba 277-8561, Japan

(Received 14 February 2005; accepted 20 June 2005; published online 4 August 2005)

The epitaxial growth of pentacene on hydrogen-terminated Si(111) is reported. Reflection high energy electron diffraction (RHEED) revealed that the crystal packing resembles that in the bulk crystal even at a monolayer thickness, which was maintained in multilayers. A ripening effect was clearly observed by atomic force microscopy (AFM). These results are important to obtain oriented crystalline films of pentacene combined with silicon microdevices with reduced defect densities.

© 2005 American Institute of Physics. [DOI: 10.1063/1.2008371]

Pentacene is one of the most promising organic semiconductors. Therefore, the epitaxial growth of pentacene is important for both application to organic electronics and fundamental studies of the conduction mechanism in molecular materials. The heteroepitaxial growth of pentacene on single crystalline surfaces is only reported for Cu(110),^{1,2} Ag(110),³ and Au(111),⁴ and the long axis of the molecules are almost parallel to the surface (“lying” orientation) for a monolayer coverage. Since the electronic conduction occurs through the interaction of π -electrons, which extends perpendicular to the long axis, it is essential to grow a film with the molecular long axis perpendicular to the surface (“standing” orientation) for its application. So far, an epitaxial thin film with a “standing” orientation is only found on Cu(110) when the film is thicker than 3.5 nm.² It has been established that the molecular packing of pentacene in thin films is different from that in a thick film or in bulk single crystals. An increased defect density is anticipated in the transition region between the thin film phase and the bulk phase, which will decrease the performance of thin film devices.

Growing organic thin films on silicon is important because silicon is easily processed by lithographic techniques. Since the Si/SiO₂ structure is actively used for microelectro-mechanical systems (MEMS) and pentacene can be used for field effect transistor (FET)-based chemical sensors,^{5,6} MEMS with sensing functions will be realized by the thin film growth of pentacene. This also opens the possibility of fabricating new devices using the lateral overgrowth of organic thin films on microcircuits made of Si and SiO₂, which will extend the single crystalline pentacene onto SiO₂ from the epitaxial seed formed on Si. The “via hole” region of pentacene can be locally removed by laser abrasion^{7,8} to make FETs with Si and SiO₂ acting as the gate electrode and the insulator, respectively.

In this paper, we describe the epitaxial growth of pentacene on hydrogen-terminated Si(111) [H-Si(111)] by ultra-high vacuum molecular beam deposition as the basis to explore the above-mentioned possibilities. Reflection high-energy electron diffraction (RHEED) and atomic force

microscopy (AFM) were used to characterize the grown thin films.

The substrate was prepared by treatment with buffered HF at 0 °C for 40 min after wet etching alternatively using boiling HNO₃ and room temperature 1% HF. It was quickly introduced into a UHV growth chamber after a final brief rinse in water. Pentacene was evaporated from a Knudsen cell by heating it at 200 °C. The growth rate was about 0.1 nm/min as measured by a quartz crystal microbalance. The substrate was kept at a certain temperature during the growth. The RHEED patterns were observed with the acceleration voltage of 20 kV using multichannel plate (MCP) detection in order to reduce the radiation damage to the films.⁹ Contact mode AFM (SEIKO SPI4000) was done under ambient conditions after remounting the sample from the vacuum chamber.

The best substrate temperature range for the epitaxial growth of pentacene was 65–80 °C. Below this range, the film tends to become amorphous and polycrystalline, while the sticking coefficient of pentacene substantially decreased above this range. For the epitaxial growth, a well-defined terrace structure of atomic height steps is necessary even within the optimal temperature range. The streak patterns of H-Si(111) became weak after the amount of deposited pentacene was 0.3–0.5-nm-thick and a halo pattern was superimposed. Thereafter, new streak patterns appeared before the thickness reached 1.5 nm. The diffraction from pentacene was clearly observed as shown in Fig. 1. In order to precisely analyze the in-plane crystal packing, the RHEED images

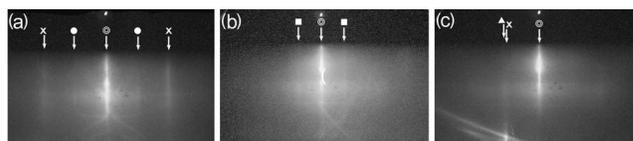


FIG. 1. RHEED images of a pentacene monolayer film grown on H-Si(111). Arrows (except for the “X”) indicate the diffraction from pentacene. The incident azimuths were parallel to Si $\langle 11\bar{2} \rangle$ (a), 9° from Si $\langle 11\bar{2} \rangle$ (b), 3° from Si $\langle 10\bar{1} \rangle$ (c). Symbols in a, b, c correspond to the reciprocal points on lines a' , b' , c' in Fig. 2(b), respectively.

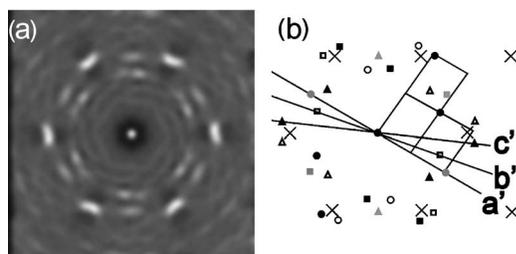


FIG. 2. (a) Two-dimensional projection of reciprocal lattice of pentacene monolayer grown on H-Si(111). (b) Assignment of the diffraction spots. “x” and other symbols correspond to the diffraction spots of Si and those of pentacene, respectively. The same symbol for pentacene belongs to the epitaxial domain with the same orientation. Lines a’, b’, and c’ indicate the reciprocal plane corresponding to RHEED images in Figs. 1(a)–1(c), respectively.

were recorded with incident azimuths rotated every 1° and were combined together to make a low energy electron diffraction (LEED)-analog two-dimensional projection. This procedure has been described elsewhere.¹⁰ Briefly, an RHEED image was integrated along the streak to obtain an intensity distribution as a function of the distance from the 00 reciprocal rod in each image. The second derivative of the function was taken to enhance the contrast, and its intensity was plotted versus the incident azimuth in the gray scale to obtain a LEED-analog image. This method offers both capabilities of *in situ* characterization during the deposition and of two-dimensional reciprocal lattice analysis.

The result is shown in Fig. 2(a), in which the spots are broadened by averaging to make the projection. Here, a six-fold symmetry was assumed to interpolate the data for the missing azimuth due to the geometry in the RHEED measurement. The LEED-analog projection can be interpreted as Fig. 2(b). From the spacing of the reciprocal lattice, it is considered that the film consists of pentacene with a “standing” orientation. Due to the crystal symmetry in the herringbone structure ordinarily found in pentacene crystals, h k diffractions with $h+k$ =odd number are expected to be weak, and in fact, were not observed in the RHEED. The diffraction of pentacene along the axis parallel to Si $\langle 10\bar{1} \rangle$ appeared at exactly half position of the substrate, which suggests the driving force of the epitaxy comes from this coincidence. As for the other primitive axis, it seems that there is no commensuration to the substrate axis. The two-dimensional lattice parameters can be determined within $\pm 0.07 \text{ \AA}$ and $\pm 1^\circ$ precision from the original RHEED images and are shown in Table I.

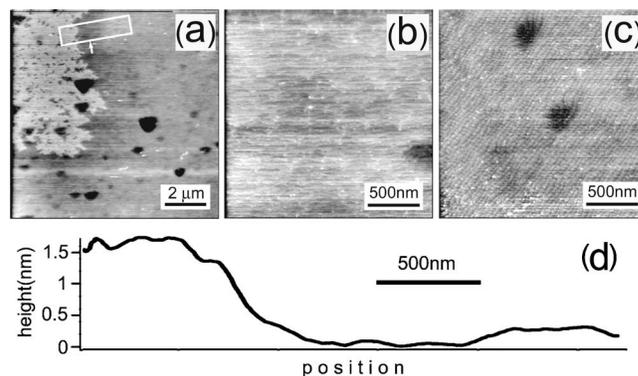


FIG. 3. (a) An AFM image of pentacene thin films formed on H-Si(111) at sub-ML coverage. (b) A magnified image $3 \mu\text{m}$ outside the island in (a). (c) AFM of H-Si(111) substrate before the growth showing a monatomic step and terrace structure. (d) Cross section of Fig. 3(a) in the white rectangle region seen from the direction of the white arrow.

The structures of the pentacene thin films have already been studied on various substrates. They are dependent on the thickness and substrate materials. Examples of structures with a “standing” orientation are summarized in Table I. It is noted that the structure determined in the present work coincides with that of the bulk crystal structure rather than those observed during the growth on other substrates. The transformation matrix¹¹ was $\begin{pmatrix} 0.949 & 1.90 \\ 1.88 & -0.243 \end{pmatrix}$ when the primitive vectors of the substrate were taken as $[-1/2 \ 1/2 \ 0]$ and $[0 \ -1/2 \ 1/2]$ of Si. Since the transformation matrix does not contain an integer element no matter what primitive lattice was chosen for the substrate, this system is categorized as incommensurate.¹¹ It fulfills point-on-line coincidence¹² condition within the experimental error because all the lattice points of the film are located on substrate lattice lines whose spacing is double of the triangular lattice constant of the substrate and whose directions are parallel to Si $[1 \ 1 \ -2]$.

An AFM image of pentacene grown on H-Si(111) with a submonolayer coverage is shown in Fig. 3(a). It clearly shows a pentacene island with an $\sim 1.5 \text{ nm}$ height, which confirms the formation of a film with a “standing” orientation. It was noted that the apparently bare substrate region outside the standing monolayer island [Fig. 3(b)] is different in morphology from the atomic-height step-and-terrace structure of the original substrate [Fig. 3(c)]. Since the background halo in RHEED increased preceding the appearance of the streak patterns from the “standing” pentacene film, the result of Fig. 3(b) suggests the formation of an amorphous pentacene adsorbate with a “lying” orientation at submono-

TABLE I. In-plane lattice parameters of pentacene layers.

Material	In-plane lattice parameters					
	a^* (\AA^{-1})	b^* (\AA^{-1})	γ^* ($^\circ$)	a (\AA)	b (\AA)	γ ($^\circ$)
Monolayer on H-Si(111) (this work)	0.159(2)	0.130(2)	96(1)	6.32(6)	7.73(7)	84(1)
Monolayer on amorphous-SiO ₂ (Ref. 13)	0.1690	0.1318	90.05	5.916	7.588	89.95
Thin film phase on glass (Ref. 14)	0.174	0.135	90	5.75	7.41	90
“Phase B” on Cu(110) (Ref. 2)	0.172	0.135	90	5.81	7.41	90
“Monolayer” of bulk (Ref. 13, 15)	0.1595	0.1286	95.32	6.266	7.775	84.68
Monolayer on carbon grid (Ref. 16)	0.1610	0.1319	89.5	6.211	7.582	91.5
Monolayer on carbon grid (Ref. 16)	0.173	0.134	89	5.78	7.46	91
Monolayer on carbon grid (Ref. 16)	0.180	0.140	89.5	5.56	7.14	90.5

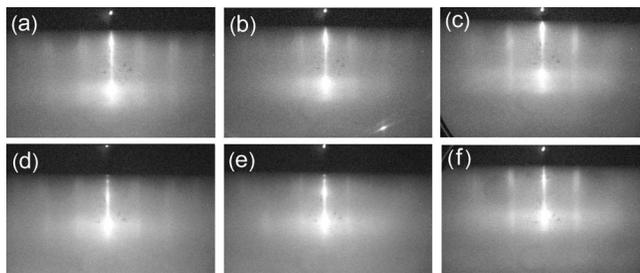


FIG. 4. RHEED image of a 5 MLE-thick pentacene film grown at 65 °C before (a, b, c) and after (d, e, f) annealing at 80 °C. The incident azimuths were Si $\langle 11\bar{2} \rangle$ (a,d), 9° from Si $\langle 11\bar{2} \rangle$ (b,e), Si $\langle 10\bar{1} \rangle$ (c,f).

layer coverage. Two possibilities then arise about what happens to the “lying” molecules after the formation of the “standing” monolayer. They may remain underneath the “standing” monolayer, or they may be totally accommodated in the “standing” monolayer. A clue to this question is found in the cross section of the AFM image at the edge of the “standing” island [Fig. 3(d)]. The cross section shows that the surface just outside the “standing” monolayer is 0.2–0.3 nm lower than the distant region. It suggests that the “lying” amorphous monolayer is absorbed to the near-by “standing” monolayer after the formation of the “standing” monolayer.

It was found that the roughness of the H–Si(111) substrate is crucial for the epitaxial growth of pentacene. When the atomic-height step-and-terrace structure was not observed, the first layer was amorphous, even if the root-mean-square roughness is less than the monoatomic height of Si(111) (0.31 nm) and the streak pattern of the substrate is observed in RHEED. Polycrystalline films were formed on the amorphous first layer when the growth was continued.

When the film thickness is increased, the epitaxial relation can be maintained up to at least 5 “standing” equivalent monolayers when the deposition was carefully continued at 65 °C with occasional annealing at 80 °C to remove the misoriented phases. Figure 4 shows the effect of the annealing. Before annealing (a–c), the superposition of the patterns corresponding to the a' and b' cross sections in Fig. 2(b) are observed in Figs. 4(a) and 4(b). The intensity of the misoriented streaks decreased after a 10-min annealing at 80 °C [Figs. 4(d) and 4(e)]. AFM images of the annealed sample are shown in Fig. 5. It shows a crystal habit with bihedral angles of 96°. It should be noted that the film morphology is different from the dendrite ones typically found in pentacene multilayer films. The almost constant distance between two crystal islands [indicated by arrows in Fig. 5(a)] and parallelogram bridging of the crystal islands [arrows in Fig. 5(b)] clearly shows the ripening of the pentacene islands, as found in the epitaxial growth of PTCDA on H–Si(111).¹⁷ It is expected that the uniformity of the crystalline films can be further improved by enhancing the ripening effect by precisely controlling the substrate temperature and the vapor pressure of pentacene on the surface.

To improve the carrier mobility of the macroscopic area, it is necessary to reduce the grain boundary caused by the symmetry mismatching between the film and the substrate. The growth of pentacene films without rotational domains is only reported for multilayers grown on Cu(110) (Ref. 2) and that on a friction-transferred polymer substrate.¹⁸ Since these

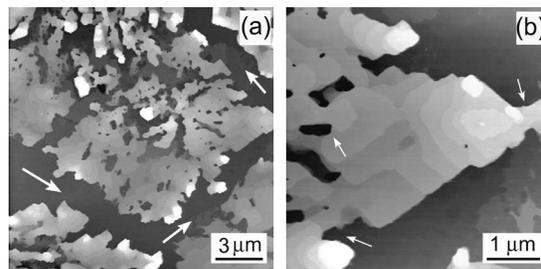


FIG. 5. AFM images of a 5 MLE-thick pentacene film after annealing. See text for the meaning of the arrows.

substrates have reduced symmetry, it is expected that the use of vicinally cut Si(111) will favorably work for improving the crystal orientation of pentacene as shown for the phthalocyanines.^{19,20}

In conclusion, the epitaxial growth of pentacene has been found on hydrogen-terminated Si(111) with atomic height steps. It was also found that the crystal structure of a monolayer thickness coincides with that of the monolayer in the bulk single crystals. The roughness of the substrate is very important for obtaining epitaxial films. Multilayers showing well-defined crystal faces can be formed on H–Si(111).

The present work was supported by MEXT, Japan. Note added in proof: We thank Dr. G. Sazaki (Tohoku Univ.) for the discussion on their recent results about pentacene monolayers epitaxially grown on H–Si(111).

- ¹S. Lukas, G. Witte, and Ch. Wöll, *Phys. Rev. Lett.* **88**, 028301 (2002).
- ²S. Lukas, S. Sohnen, G. Witte, and Ch. Wöll, *ChemPhysChem* **5**, 266 (2004).
- ³Y. L. Wang, W. Ji, D. X. Shi, S. X. Du, C. Seidel, Y. G. Ma, H.-J. Gao, L. F. Chi, and H. Fuchs, *Phys. Rev. B* **69**, 075408 (2004).
- ⁴P. G. Schroeder, C. B. France, J. B. Park, and B. A. Parkinson, *J. Appl. Phys.* **91**, 3010 (2002).
- ⁵T. Minakata, *Polym. Adv. Technol.* **6**, 607 (1995).
- ⁶C. K. Song, B. W. Koo, and M. K. Jung, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **270**, 337 (2001).
- ⁷I. Yagi, K. Tsukagoshi, and Y. Yoshinobu, *Appl. Phys. Lett.* **84**, 813 (2004).
- ⁸R. Parashkov, E. Becker, G. Ginev, T. Riedl, M. Brandes, H. H. Johannes, and W. Kowalsky, *Appl. Phys. Lett.* **85**, 5751 (2004).
- ⁹K. Saiki, T. Kono, K. Ueno, and A. Koma, *Rev. Sci. Instrum.* **71**, 3478 (2000).
- ¹⁰H. Ichikawa, T. Shimada, and A. Koma, *Jpn. J. Appl. Phys., Part 1* **40**, L225 (2001).
- ¹¹D. E. Hooks, T. Fritz, and M. D. Ward, *Adv. Mater. (Weinheim, Ger.)* **13**, 227 (2001).
- ¹²A. Hoshino, S. Isoda, H. Kurata, and T. Kobayashi, *J. Appl. Phys.* **76**, 4113 (1994).
- ¹³S. E. Fritz, S. M. Martin, C. D. Frisbie, M. D. Ward, and M. F. Toney, *J. Am. Chem. Soc.* **126**, 4084 (2004).
- ¹⁴T. Minakata, H. Imai, M. Ozaki, and K. Saco, *J. Appl. Phys.* **72**, 5220 (1992).
- ¹⁵D. Holmes, S. Kumaraswamy, A. J. Matzger, and K. P. C. Vollhardt, *Chem.-Eur. J.* **5**, 3399 (1999).
- ¹⁶C. C. Mattheus, A. B. Dros, J. Baas, G. T. Oostergetel, A. Meetsma, J. L. deBoer, and T. T. M. Palstra, *Synth. Met.* **138**, 475 (2003).
- ¹⁷G. Sazaki, T. Fujino, N. Usami, T. Ujihara, K. Fujiwara, and K. Nakajima, *J. Cryst. Growth* **273**, 594 (2005).
- ¹⁸H. Kihara, Y. Ueda, A. Unno, and T. Hirai, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **424**, 195 (2004).
- ¹⁹T. Shimada, A. Suzuki, T. Sakurada, and A. Koma, *Appl. Phys. Lett.* **68**, 2502 (1996).
- ²⁰M. Nakamura, T. Matsunobe, and H. Tokumoto, *J. Appl. Phys.* **89**, 7860 (2001).

Applied Physics Letters is copyrighted by the American Institute of Physics (AIP).
Redistribution of journal material is subject to the AIP online journal license and/or AIP
copyright. For more information, see <http://ojps.aip.org/aplo/aplcr.jsp>