Vol 17 No 10, October 2008
1674-1056/2008/17(10)/3822-05

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

The effect of annealing temperature and film thickness on the phase of pentacene on the p^+-Si substrate*

Yuan Guang-Cai(袁广才), Xu Zheng(徐 征)†, Zhao Su-Ling(赵谡玲), Zhang Fu-Jun(张福俊), Huang Jin-Zhao(黄金昭), Huang Jin-Ying (黄金英), Tian Xue-Yan(田雪雁), and Xu Xu-Rong (徐叙瑢)

Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, *China*
Key Laboratory of Luminescence and Optical Information (Beijing Jiaotong University), Ministry of Education, Beijing 100044, *China*

(Received 14 November 2007; revised manuscript received 11 April 2008)

This paper investigates the morphology and crystallization properties of the two crystalline phases of pentacene grown by thermal evaporation on p^+-Si substrates at room temperature by the methods of atomic force microscopy and x-ray diffraction. This kind of substrate induces a thin film phase and a triclinic phase which are formed directly onto p^+-Si substrates and constitute a layer consisting of faceted grains with a step height between terraces of 15.8 Å (1 Å=0.1 nm) and 14.9 Å, respectively. Above the critical thickness of the thin film phase, lamellar structures are found with an increasing fraction with the increase of the film thickness. When the film thickness is fixed, the fraction of lamellar structures increases with the increase of annealing temperature. These lamellar structures are identified as the second phase with a interplanar distance of 14.9 Å corresponding to the pentacene triclinic phase. Furthermore, the thin film phase consisting of several micrometre sized uniformly oriented grains at an annealing temperature of less than 80°C and a deposition rate of 0.6 Å/s is observed.

Keywords: pentacene, morphology, crystalline phase, thin-film transistors
PACC: 6110M, 6170A, 6855, 6890

1. Introduction

Organic thin-film transistors (OTFTs) are of interest for the fabrication of low-cost, mass-produced electronics using flexible substrates and low-end electronics. The performance of OTFTs has been improved significantly in the past decade and already reached a comparable status to hydrogenated amorphous silicon transistors (*a*-Si:H TFT).[1−4] OTFTs is a powerful experimental tool to investigate the charge carrier transport properties of organic materials, including the density of states distribution, charge carrier mobility and stability. Pentacene is an interesting semiconducting organic material for use in OTFTs.[5−7] Recently, many articles attempted to explain the temperature dependence of the charge carrier mobility in terms of a fundamental transport mechanism, which were ascribed to traps and/or contact effects. Besides these effects, the thin film morphology and the organic molecular crystal structure also are crucial parameters for the OTFT characteristics. From x-ray diffraction (XRD) and atomic force microscopy (AFM) studies, it is shown that thermal evaporated pentacene thin films typically consist of two crystalline phases and two layer structures with different monomolecular step height.[8−10]

In this work we present our experimental investigations on the properties of pentacene thin films grown by means of thermal evaporation on p^+-Si surfaces. Firstly, morphologies of two crystalline phases of pentacene are investigated and the influence of annealing temperature and thickness is compared. Finally, we obtained the dependence of the crystalline phase on the film thickness and annealing temperature.

*Project supported by the National High Technology Research and Development Program (863 plan) of China (Grant No 2006AA03Z0412), the National Natural Science Foundation of China (Grant Nos 60576016 and 10774013), the Excellent Doctor's Science and Technology Innovation Foundation of Beijing Jiaotong University (Grant No 48024), The Research Fund for the Youth Scholars of the Doctoral Program of Higher Education (Grant No 20070004031), the Beijing NOVA program (Grant No 2007A024), the Project Sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry; the Foundation of Beijing Jiaotong University (Grant No 2005SM057).
†Corresponding author. E-mail: zhengxu@bjtu.edu.cn or ygc219@126.com

2. Experimental

In order to investigate the potential of pentacene as the active layer of OTFTs, firstly we prepared pentacene films with different thickness on highly doped p^+-Si wafer substrates. p^+-Si substrates were cleaned with acetone, ethanol, and deionized water in this particular order by ultrasonics. These different thick pentacene films ($J\&K$ Chem. Co. 98% used without any further purification) from a quartz boat with a lid through two small holes (3 mm diameter) were deposited onto p^+-Si wafers at a pressure of 2.5×10^{-5} Pa by the thermal evaporation. The evaporation rate of pentacene and the substrate temperature were 0.6 Å/s and room temperature, respectively. The thicknesses of pentacene are 80 nm, 100 nm, 120 nm and 150 nm, respectively. Then all samples were annealed for 120 minutes at different temperature in the vacuum oven at 1.0×10^{-1} Pa. Finally, the surface morphology and crystallization of pentacene thin films were measured by AFM, and XRD, respectively.

3. Results and discussion

The pentacene thin films were deposited on highly doped p^+-Si wafers and annealed at different temperature between 40°C and 120°C. Through XRD measurement, an increase of the ratio between the two observed diffraction peaks was observed in the pentacene films with the thicknesses of 120 nm and 100 nm respectively, as shown in Fig.1. While pentacene was deposited at room temperature, its XRD consists of the thin film phase completely and is characterized by one set of diffraction peaks in XRD spectra with interplanar distance of 15.8Å (phase 1). The increase of the annealing temperature introduces a second set of diffraction peaks with interplanar distance of 14.9 Å (phase 2), which is attributed to the pentacene triclinic phase. Annealed at 110°C the first order diffraction peak of both phases of pentacene is equal.

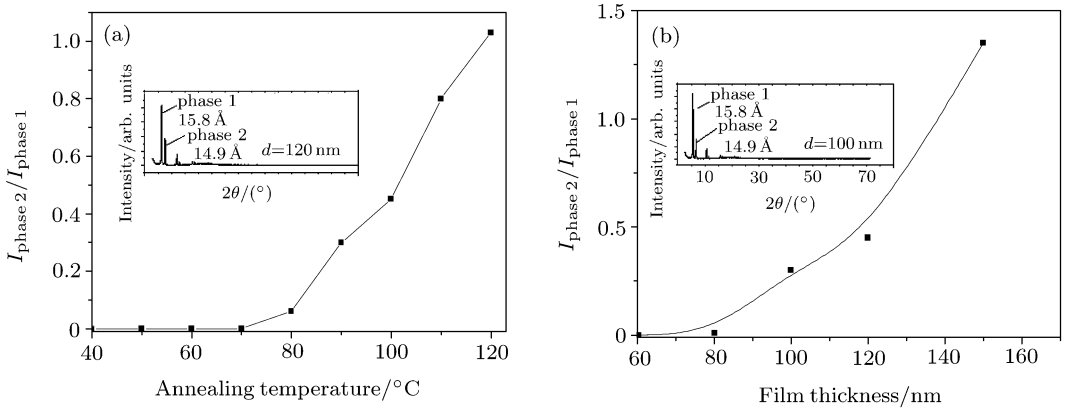


Fig.1. The inset shows a typical XRD spectrum of a thermal evaporated pentacene, thin film thickness 120 nm (a) and 100 nm (b), annealing temperature of 80°C on p-Si, indicating two crystallographic phases with a interplanar distance of 14.9 Å and 15.8 Å, respectively. Furthermore, the ratio of the intensity of the first order diffraction peak of phase 2 relative to phase 1 is shown as a function of annealing temperature and thin films thickness of pentacene thin film.

In order to confirm and identify both pentacene thin film phases, we analysed thin films deposited at a constant deposition rate (0.6 Å/s) and annealed at a constant temperature (80°C with various thicknesses. The obtained XRD spectra of these films are shown in Fig.2. An increase of the ratio between two observed first order diffraction peaks in XRD scans, as shown in Fig.1, is observed. Then, a varying ratio between these diffraction peaks of both phases was detected again. The film thickness is incrassate; the intensity of the set of peaks corresponding to the triclinic phase enhances.[11,12]

The XRD data show that the pentacene triclinic phase appears after a critical thickness of the thin film phase and the fraction of triclinic phase increases with the film thickness (shown in Fig.2).[13] The critical thickness of the thin film phase is strongly dependent on the annealing temperature. For a room temperature substrate, the critical film thickness decreases with the increasing annealing temperature. At an annealing temperature of 80°C, the critical film thickness is about 80 nm (shown in Fig.1.(a)). These results

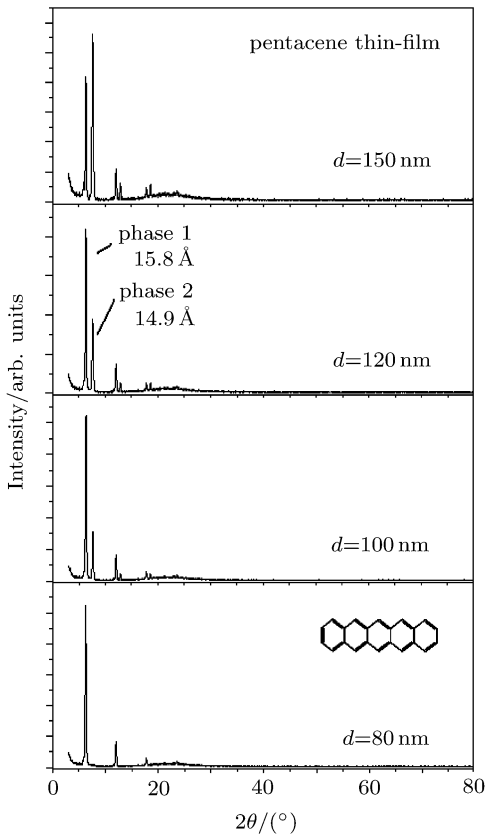


Fig.2. XRD spectra of pentacene films with thicknesses d of 80 nm, 100 nm, 120 nm and 150 nm deposited at a substrate temperature of room temperature. At a film thickness of 150 nm, the triclinic phase diffraction peak has become the dominant phase. In contrast to the XRD spectrum of very thin film of 80 nm thickness, the thin film phase is the only contribution.

indicate that the thin film phase is a substrate and annealing temperature induced phase, the critical film thickness of this phase is strongly dependent on the film thickness at a fixed substrate temperature (shown in Fig.1(b)). The analysis shows an increasing fraction whose AFM patterns turn out that pentacene has a lamellar-like structure (shown in Fig.3(b)) with the increased annealing temperature. When the annealing temperature is lower than 80°C, this lamellar like structure of pentacene is not observed completely at same condition. This suggests that the lamellar-like structure can be identified as the triclinic phase of pentacene

AFM patterns of the films with layer thicknesses of 80 and 100 nm are shown in Fig.3.[14] The film consisting only of the thin film phase (shown in Fig.3(a)) shows uniformly distributed 1.5–2.0 μm sized grains with strong faceting behaviour. These grains have a layered structure with a monomolecular step height of roughly 1.5 nm which corresponds to the interplanar distance of 15.8 Å as observed in the XRD spectra (shown in Fig.4(a)). The faceting behaviour is observed at every separate terrace and oriented along the same crystallization direction, indicating a preferential growth direction of the crystallite. The faceting directions are along the $[1\bar{1}0]$ and the [110] unit cell direction corresponding to the herringbone directions,[15] as observed with molecular resolved images on one terrace (shown in Fig.4(b)).

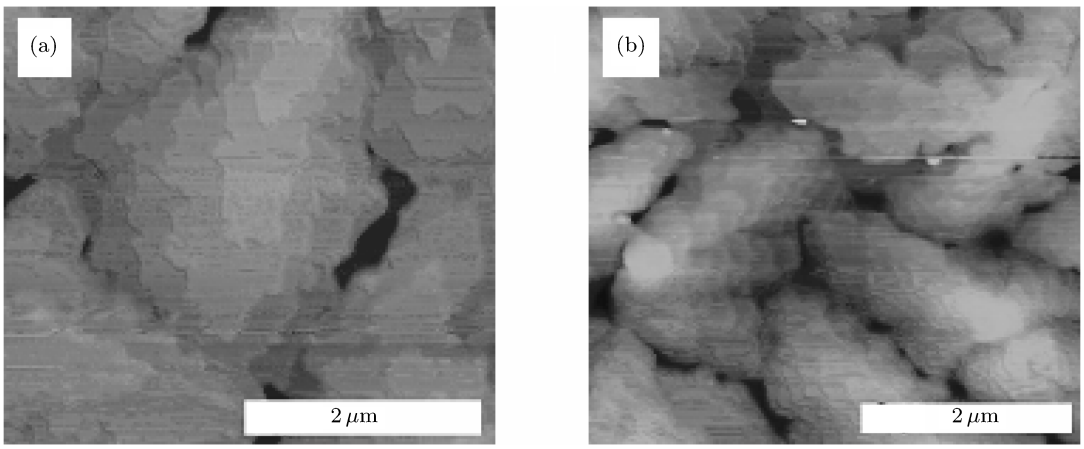


Fig.3. AFM patterns of pentacene thin films at deposited film thickness of (a) 80 nm showing faceted terrace-like thin layers of the pentacene thin film phase and (b) 100 nm showing lamellar-like structures, which is attributed to the pentacene bulk phase; the background morphology is thin film ordered phase.

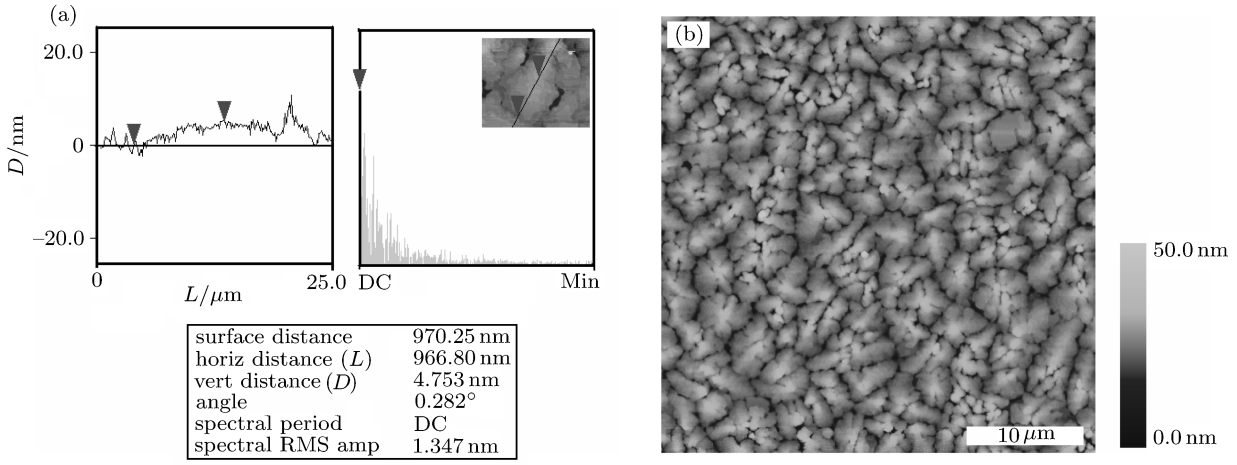


Fig.4. (a) The section analysis spectrum of grains layered structure with a monomolecular step height of roughly 1.5 nm which corresponds to the interplanar distance of 15.8 Å (D is scanning vertical distance, L is scanning horizontal distance) and (b) AFM images of pentacene thin films at deposited film thickness of 80 nm showing the herringbone-like directions thin layers of the pentacene thin film.

According to the molecular resolved image, we estimate that the axis values (a and b) of the in-plane unit cell of the thin film phase are comparable with the values known for triclinic phase pentacene. From this we conjecture that the major difference between the thin film phase and the triclinic phase is the length and orientation of the c-axis in the unit cell. AFM patterns of films with a thickness above the critical thickness reveal that pentacene molecules like lamellar-like plates (Fig.3(b)) with a length of 1.5–3.0 μm. The density of these lamellar-like structures is observed to increase with the increase of the film thickness.

The observed two crystalline phases in XRD spectra can now be identified with the corresponding morphology by using the AFM and XRD measurements. The increase of the lamellar-like structures with the film thickness as observed by AFM together with the increase of phase 2 in the XRD spectra lead to the conclusion that the lamellar-like structures can be identified as pentacene triclinic phase. The thin film phase is characterized by strongly facetted grains and initially grows onto the substrate with a critical film thickness which is dependent on the annealing temperature. The size of the grains of the thin film phase (Fig.3(a)) is strongly dependent on the evaporation parameters. Both the increase of annealing temperature (40 to 120°C) and the decrease of the deposition rate at a constant temperature yield an increase of the size of the individual grains (1–2 μm) which are uniformly oriented with the same azimuthal orientation with respect to the substrate plane. We believe that the obtained OTFTs with high mobility are likely to consist solely of the thin film phase. Ideally, one would like to use these single phased pentacene transistors in order to study the fundamental transport properties.[15]

4. Conclusions

In this paper we have experimentally identified the morphology of the two crystalline phases which exist in thermal evaporated pentacene thin films on p^+-Si substrates. We show that a thin film phase is formed directly onto the p^+-Si substrate, which induces a layer consisting of faceted grains with an interplanar distance of 15.8 Å. Above a critical film thickness, the thin film phase is dependent on the annealing temperature. And lamellar-like structures are found with an increasing fraction as a function of the film thickness. These structures are identified as the second phase, and are attributed to the pentacene triclinic phase with an interplanar distance of 14.9 Å. Therefore we could obtain single phase pentacene based OTFTs with high mobility through controlling the annealing temperature and the film thickness.

References

[1] Han S H, Kim J H, Janga J, Cho S M, Myung H O, Lee S H and Choo D C 2006 *Appl. Phys. Lett.* **88** 073519

[2] Bana D, Han S, Lu Z H, Oogarah T, SpringThorpe A J and Liu H C 2007 *Appl. Phys. Lett.* **90** 093108

[3] Ma M R, Chen Y L and Wang C 2006 *Chin. Phys.* **15** 2657

[4] Xia Z L, Du G, Liu X Y, Kang J F and Han R Q 2007 *Chin. Phys.* **16** 0537

[5] Zhang F J, Aollmer A, Zhang J, Xu Z, Rabe J P and Koch N 2007 *Organic Electronics* **8** 606

[6] Liu H X, Hao Y, Hawkins I D and Peaker A R 2005 *Chin. Phys.* **14** 1644

[7] Hulea I N, Fratini S, Xie H, Mulder C L, Iossad N N, Rastelli G, Ciuchi S and Morpurgo A F 2006 *Nature Materials* **5** 982

[8] Yun M, Gangopadhyay S, Bai M, Taub H, Arif M and Guha S 2007 *Organic Electronics* **8** 591

[9] Schoonveld W A, Vrijmoeth J and Klapwijk T M 1998 *Appl. Phys. Lett.* **73** 3884

[10] Zheng Z S, Liu Z L, Zhang G Q, Li N, Fan K, Zhang E X, Yi W B, Chen M and Wang X 2005 *Chin. Phys.* **14** 0565

[11] Parisse P, Picozzi S and Ottavianom L 2007 *Organic Electronics* **8** 498

[12] Bouchoms I P M, Schoonveld W A, Vrijmoeth 1 J and Klapwijk T M 1999 *Synthetic Metals* **104** 175

[13] Mascaro D J 2001 *IBM J. Res. Dev.* **5** 10

[14] Lin Y Y, Gundlach D J, Nelson S F and Jackson T N 1997 *IEEE Electron Device Letters* **18** 606

[15] Knipp D and Street R A 2004 *J. Non-Crystalline Solids* **338–340** 595