Growth Mode of PTCDA on p-Si Substrates

Song Zhen[1,†], Ou Guping[2], and Liu Fengmin[1]

(1 *College of Science, Beijing Information Science & Technology University, Beijing* 100085, *China*)
(2 *School of Physics, Human University of Science and Technology, Xiangtan* 411201, *China*)

Abstract: AFM scanning images of the surface of a PTCDA/p-Si specimen used in an organic/inorganic photodetector show that PTCDA grows in island shapes that are poorly distributed, with each island shaped like a round hillock. The images also show that there exist enormous defects in the PTCDA layer due to pedestal sites and other defects that appear when Si atoms shift transversely, and that the bonding condition is satisfied by the action of atom suspension bonding at the surface of the Si substrate. We infer the growth mode of PTCDA deposited onto p-Si substrates as follows. First, PTCDA molecules assemble at the defects to form three-dimensional island-like PTCDA crystal nuclei, and then by the action of delocalized big π bonding, two adjacent layers of PTCDA molecules overlap to some extent and finally island-like structures form. The PTCDA molecules and Si substrate combine by a process of the combination of benzene rings with Si atoms at the defects and of acid anhydride radicals with Si atoms at the perfect fraction of the surface. In the course of combination, although the structure of the benzene rings does not change, the chemical reaction of acid anhydride radicals and Si occurs to break off the C=O bond in the acid anhydride, and then C—Si—O and silicon oxide might be produced.

Key words: PTCDA; growth mode; AFM
EEACC: 2530N
CLC number: TN304 **Document code**: A **Article ID**: 0253-4177(2007)07-1009-03

1 Introduction

The prominent characteristic of organic films as electrical materials is that they are not well lattice-matched with inorganic semiconductors. Experiments suggest that the organic semiconductor PTCDA can form an ordered layer with a monoclinic structure at the surface of monocrystalline silicon. In a vacuum, PTCDA is sublimed onto a polished, non-oxidized Si substrate, and its deposited film orients as easily as possible. Therefore PTCDA has been widely applied in the field of photoelectronics[1~3].

The molecular structure of PTCDA ($C_{24}H_8O_6$) is shown in Fig. 1. It is a wide band-gap organic semiconductor with two molecules in a monoclinic unit cell with an overlap distance between the two molecules of 0.321nm. In addition, its valence and first tight-binding conduction band are separated by an energy of 2.2eV. At room temperature, the hole density of highly ordered PTCDA film is $5\times10^{14}\ cm^{-3}$, and the hole mobility perpendicular to the substrate ranges from 10^{-7} to $10^{-6}\ cm^2/(V\cdot s)$[4]. It is also transparent at the wavelength of 632.8nm.

At the interface of vacuum-deposited PTCDA by sublimation onto p-Si substrate, a dipole layer of space charge——a heterojunction barrier——forms due to the differences in the forbidden gap, electronic affinity energy, work function, and dielectric constants between the two kinds of semiconductors[5]. At high reverse voltage (about 240V), organic/inorganic photodetectors made from PTCDA/p-Si have very low current (about $10^{-9}\ A/cm^2$) and are very sensitive to visible light and near infra-red light[6]. We here report the growth mode of PTCDA sublimation onto p-Si substrates using atomic force microscopy (AFM).

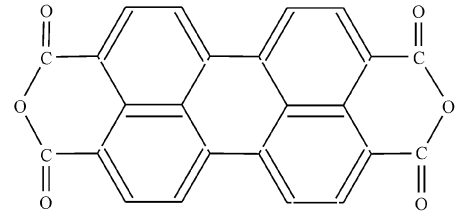

Fig. 1 Molecular structure of PTCDA

† Corresponding author. Email: songzhe9824@sina.com.cn
Received 8 February 2007, revised manuscript received 16 March 2007

Experiments have shown that the quality of this kind of photodetector has much to do with the thickness of the organic layer and its pattern[7].

2 Experiments

In order to fabricate the PTCDA/p-Si specimen, 99.5% purified PTCDA was deposited by vacuum sublimation at $<10^{-4}$ Pa onto p-Si(100) substrates with a resistivity of 0.2Ω·m and a carrier density of $2.6\times10^{16}\,cm^{-3}$. The (101) planes of the PTCDA on the substrate were inclined by 11° and had a thickness of 160nm.

Surface patterns were obtained by scanning the surface of the PTCDA/p-Si specimen using a Topometrix Explorer AFM scanner, as shown in Figs. 2 (a) and (b), where the shade of gray represents the height in the direction perpendicular to the surface. The lighter the shade of gray is, the more drastically the profile undulates in the z direction. The areas scanned by AFM were $0.10\mu m\times0.10\mu m$ and $2.5\mu m\times2.5\mu m$, respectively.

3 Results and discussion

As shown in Fig. 2(a), PTCDA grows in island shapes that are poorly distributed, with each island being in the shape of a round hillock, 50～70nm in diameter and 3～7nm in height, which indicates that the islands are different from each other to some extent. The flat-image of AFM in Fig. 2(a) was divided into 25 squares, each with an area of $0.5\mu m\times0.5\mu m$. By calculating the island density of each area, we obtain an average island density of $68\mu m^{-2}$ with a mean deviation of $7\mu m^{-2}$, which reflects that the islands were poorly distributed. As Figure 2(b) shows, the islands were spine-like aligned due to the difference of the scanning area and normal scale. In addition, it was found that there existed enormous defects in the PTCDA layer, due to pedestal sites and other defects appearing when Si atoms shift transversely and the bonding condition is satisfied by the action of atomic suspension bonding at the surface of the Si substrates. There are a group of very irregular pedestal sites and many flexural fragments[8]. Crystal nuclei form at the defects prior to other places since the binding energy of external atoms and defects is larger than that of external atoms and the perfect surface[9]. For the deposited PTCDA, crystal nuclei form at the defects prior to other places too. Furthermore, the poor distribution of defects leads to the poor distribution of PTCDA crystal nuclei and then results in the poor distribution of islands. From the existence of pedestal sites and flexural fragments, it is inferred that PTCDA grows at the surface of p-Si by three dimensional growth mode (Volmer-Weber). First, many three-dimensional island-like PTCDA crystal nuclei form on the p-Si substrate, and then two adjacent layers of PTCDA molecules overlap to some extent by the action of delocalized big π bonding. Finally, the island-like structures form[10]. The gathering of PTCDA molecules at the defects of the Si surface is one of reasons for the large surface leakage current of organic/inorganic photodetectors.

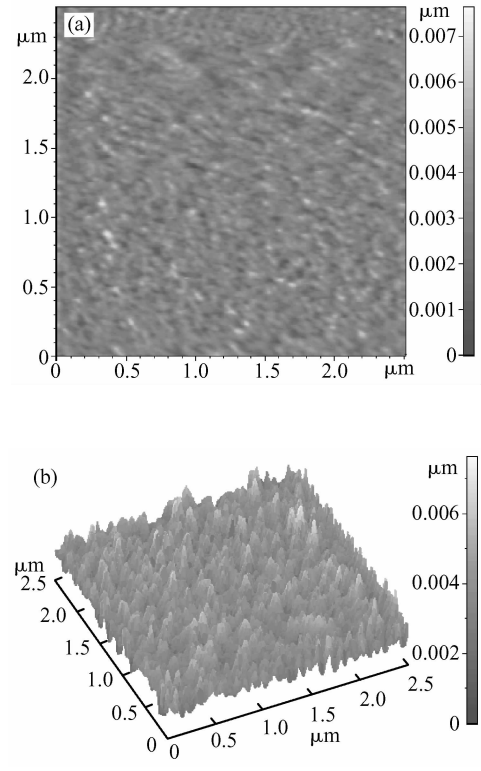

Fig. 2 AFM micrographs of the PTCDA/p-Si surface (a) Lateral force mode; (b) Topographic mode

4 Conclusion

AFM scanning images of the surface of a PTCDA/p-Si specimen suggest that PTCDA grows as island shapes that are poorly distributed, with each island shaped as a round hillock. The images

also show that there exist enormous defects in the PTCDA layer due to pedestal sites and other defects that appear when Si atoms shift transversely and that the bonding condition is satisfied by the action of atomic suspension bonding at the surface of the Si substrate. It is inferred that PTCDA grows at the surface of p-Si by three dimensional growth mode(Volmer-Weber). The PTCDA molecules and Si substrate combine by a process of the combination of benzene rings with Si atoms at the defects and of acid anhydride radicals with Si atoms at the perfect fraction of the surface. In the course of combination, although the structure of the benzene rings does not change, the chemical reaction of acid anhydride radicals and Si occurs to break off the C═O bond in the acid anhydride, and then C—Si—O and silicon oxide might be produced.

References

[1] Forrest S R, Zhang Y. Ultrahigh-vacuum quasiepitaxial growth of model van der Waals thin films: I Theory. Phys Rev B, 1994, 49(16): 11297

[2] Forrest S R, Burrows P E, Haskal E I, et al. Ultrahigh-vacuum quasiepitaxial growth of model van der Waals thin films: II Experiment. Phys Rev B, 1994, 49(16): 11309

[3] Möbus M, Karl N. Structure of perylene-tetracar-boxylic-dianhydride thin films on alkah halide crystal substrates. J Cryst Growth, 1992, 116(2): 495

[4] Mathine D L, Woo H S, He W. Heterogeneously integrated organic light-emitting diodes with complement arymetal-oxide-silicon circuitry. Appl Phys Lett, 2000, 76(26): 3849

[5] Zhang Fujia, Wang Deming, Zhang Dejiang, et al. Investigation on barrier characteristics for Si-based compounds. Chinese Semiconductor Optoelectronics, 2000, 21(3): 182

[6] Zhang Fujia, Shao Jiafeng, Zhang Dejiang, et al. Preparation of organic semiconductor PTCDA and studies on its structure indication and specific property of light absorption. J Luminescence, 1999, 20(4): 351(in Chinese)[张福甲, 绍佳峰, 张德江, 等. 有机半导体材料 PTCDA 的制备和结构表征以及特殊感光性质的研究. 发光学报, 1999, 20(4): 351]

[7] Zhang Fujia, Wang Deming. The formation of PTCDA/p-Si heterojunction barrier potential and the analysis of transmission mechanism for its electric current. Journal Gansu Sciences, 2000, 12(1): 1(in Chinese)[张福甲, 王德明. PTCDA/p-Si 异质结势垒的形成以及电流传输机制的分析. 甘肃科学, 2000, 12(1): 1]

[8] Tu K N, Mayer J W, Feldman L C. Electronic thin film sciences: for electrical engineers and material scientists. America: Macmillan College Publishing Company Inc Press, 1992

[9] Wu Ziqin, Wang Bing. Film growth. Beijing: Science Press, 2001 (in Chinese)[吴自勤, 王兵. 薄膜生长. 北京: 科学出版社, 2001]

[10] Cheng L F, Liao L S, Lai W Y, et al. Effect of deposition rate on the morphology, chemistry and electroluminescence of tris-(8-hydroxyquinoline) aluminum films. Chem Phys Lett, 2000, 319(12): 418

p-Si 基 PTCDA 的生长模式

宋　珍[1,†]　欧谷平[2]　刘凤敏[1]

(1 北京信息科技大学理学院, 北京　100085)
(2 湖南科技大学物理学院, 湘潭　411201)

摘要: 对有机/无机光电探测器 PTCDA/p-Si 样品表面进行 AFM 测试, 结果表明 PTCDA 呈岛状生长, 各岛成圆丘状, 岛的分布不均匀, PTCDA 层中存在大量缺陷. 原因是 p-Si(100)衬底的表面原子悬挂键的作用, 使硅原子横向移动满足键合需要形成台阶和其他缺陷. 得出 PTCDA 在 p-Si 基底上的生长模式为: PTCDA 首先在缺陷处聚集, 形成许多三维岛状的 PTCDA 晶核, 然后在 PTCDA 离域大 π 键的作用下, 相邻的两层 PTCDA 分子存在一定程度的交叠, 最终形成岛状结构.

关键词: PTCDA; 生长模式; AFM
EEACC: 2530N
中图分类号: TN304　　**文献标识码:** A　　**文章编号:** 0253-4177(2007)07-1009-03

† 通信作者. Email: songzhe9824@sina.com.cn

2007-02-08 收到, 2007-03-16 定稿