Available online at www.sciencedirect.com
SCIENCE DIRECT
Surface Science 600 (2006) 2518–2522
SURFACE SCIENCE
www.elsevier.com/locate/susc

In-situ measurement of molecular orientation of the pentacene ultrathin films grown on SiO_2 substrates

Genki Yoshikawa [a,*], Tetsuhiko Miyadera [a], Ryo Onoki [b], Keiji Ueno [b], Ikuyo Nakai [a], Shiro Entani [c], Susumu Ikeda [c], Dong Guo [c], Manabu Kiguchi [d], Hiroshi Kondoh [a], Toshiaki Ohta [a], Koichiro Saiki [a,c]

[a] *Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[b] *Department of Chemistry, Faculty of Science, Saitama University, Shimo-Okubo 255, Saitama 338-8570, Japan*
[c] *Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwa-no-ha, Kashiwa, Chiba 277-8561, Japan*
[d] *Department of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan*

Received 13 January 2006; accepted for publication 7 April 2006
Available online 11 May 2006

Abstract

Molecular orientations of pentacene ultrathin films grown on SiO_2 substrates were studied without the influence of the atmosphere by vacuum atomic force microscopy (V-AFM) and near edge X-ray absorption fine structure (NEXAFS). The experimental processes from deposition of pentacene to characterization of films were performed under vacuum condition without exposure to the atmosphere. V-AFM and NEXAFS measurements showed that pentacene molecules tend to grow on SiO_2 surface with their molecular long axes perpendicular to the substrate surfaces (standing-mode) irrespective of preparation procedure of SiO_2 substrate.

Keywords: Pentacene; In-situ characterization; Atomic force microscopy; Near edge extended X-ray absorption fine structure (NEXAFS); Surface structure, morphology, roughness and topography; Silicon oxides; Aromatics; Thin film structures

1. Introduction

Pentacene has been receiving an increasing amount of attention in recent years. The interest can be attributed to its promising potential for flexible and low-cost electronic devices, especially for organic field effect transistors (OFET). Among all channel materials for organic thin film transistors studied so far, pentacene shows the highest carrier mobility [1]. Thereby, there have been numerous reports investigating electrical and morphological properties of pentacene thin films grown on gate insulator materials, mostly SiO_2 substrates [1,2]. Recently, our group revealed that an accumulation layer in the bottom-contact FET structure is limited within the first several pentacene layers from the pentacene–SiO_2 interface [3]. This result teaches us that the molecular orientation at the initial stage of growth strongly affects the FET performance. Thus, its characterization would provide useful information on improvement of FET performance, which is still poor as compared with inorganic semiconductors. In order to clarify the orientation of the molecules in the first few layers, a surface sensitive tool is necessary. In the commonly used bottom-contact FET structure, however, electron beam could not be used as the probe because the insulating nature of substrate causes a charge build-up problem. Thereby, conventionally used surface sensitive techniques such as electron diffraction, scanning tunneling microscope, etc. do not work well for that purpose.

* Corresponding author. Present address: Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan. Tel.: +81 22 2152023; fax: +81 22 2152020.
E-mail address: yoshik-0@imr.tohoku.ac.jp (G. Yoshikawa).

0039-6028/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2006.04.012

Recently, some studies, in which electron was not used as the probe, have been reported on the first monolayer of the pentacene film grown on a SiO_2 substrate [4–6]. Using grazing incidence X-ray diffraction (GIXD) and atomic force microscopy (AFM), they showed that the pentacene molecules grew with their molecular long axes perpendicular to the surface. Diffraction measurement such as GIXD, however, can probe only the molecules in order, so that the degree of ordering of the whole film can not be known only by the diffraction method. AFM, on the other hand, is a powerful tool to obtain the whole structure of the ultrathin film from a morphological viewpoint, although the molecular orientation could not be usually determined.

Another problem relates with the effect of atmosphere. In most of the past works, the pentacene films were characterized after putting them out from the vacuum chamber. Organic materials, especially in an ultrathin film state, are susceptible to H_2O, O_2, and other environmental elements present in the atmosphere. No one could exclude the possibility that the structure of a pentacene film would have changed by exposure to air, because there is no strong interaction such as chemical bond between a pentacene molecule and an inert SiO_2 substrate of amorphous structure. Actually, many studies have been reported about the influence of these gases on OFET properties [7–9], suggesting the occurrence of any structural change. Qiu et al. have reported that the pentacene FET was significantly degraded by H_2O and the morphology of the film changed after the transistor had been kept in the atmosphere [10]. Accordingly, with respect to the molecular orientation of pentacene ultrathin films on SiO_2, it has not been recognized yet whether the observed structure is truly as-grown one or changed by the influence of the atmosphere. Therefore, the elucidation of the molecular orientation of a pentacene ultrathin film without the influence of the atmosphere is important not only for the fundamental research but also for the application.

In the present study, we present the experimental results on the molecular orientation in a monolayer pentacene film, which was characterized without exposure to air. We constructed a vacuum AFM (V-AFM) system, in which all procedures, from deposition on SiO_2 substrates to the AFM measurement, can be done under vacuum condition. Hence, the V-AFM can measure the film morphology at the initial stage of growth without the influence of the atmosphere. In addition, we connected the deposition chamber directly to the synchrotron radiation (SR) facility and measured the near edge X-ray absorption fine structure (NEXAFS) of an as-grown pentacene film, probing the molecular orientation of all the pentacene molecules in the film.

2. Experimental details

The experiments were performed in a custom-designed UHV system with a base pressure of 10^{-7} Pa. In order to confirm the influence of charge build-up or the preparing condition of the substrates, three types of SiO_2 substrates were used; prepared by oxidation of a Si wafer with Shiraki method [11], Shiraki method and following anneal in dry O_2, and a commercially obtained Si wafer with thermally oxidized amorphous SiO_2 layer. The thickness of SiO_2 layer of these substrates is 1.5 nm, 10 nm, and 300 nm. All the substrates were rinsed in acetone and ultra pure water before loading into vacuum chamber without succeeding annealing in the growth chamber. Pentacene molecules were evaporated from a Knudsen-cell onto the substrates maintained at 298 K. Growth rate and the mean film thickness were monitored using a quartz crystal oscillator, and the rate was on the order of 0.1 nm/min. Grown films were transferred to the directly connected AFM chamber without exposure to the atmosphere. V-AFM images were recorded in the tapping mode with JEOL JSPM-5200 V. C K-edge NEXAFS measurement was carried out at the BL-7A of the Photon Factory in the Institute of Materials Structure Science [12]. The sample grown in the deposition chamber was transferred to the manipulator at the BL-7A station without breaking vacuum. C K-edge NEXAFS spectra were then obtained in situ by the partial electron yield method with a micro-channel plate. The degree of the beam polarization was estimated to be 0.92.

3. Results and discussion

Fig. 1 shows the V-AFM image and its height profile of a pentacene film deposited on a commercially obtained amorphous SiO_2 substrate. The mean film thickness was about 0.2 nm. Pentacene films deposited on the SiO_2 substrates prepared by Shiraki-method showed similar V-AFM images. The height of pentacene islands is uniquely determined to be 1.6 nm in close agreement with the molecular long axis of a pentacene molecule (1.65 nm). Therefore, it is not unreasonable to consider that pentacene molecules were grown with standing-mode (cf. Fig. 2). This result is consistent with the previous result measured by GIXD [4]. There were several reports investigating the monolayer pentacene film by AFM in the atmosphere. They also indicated the standing-mode similar as shown in Fig. 2. The significance of the present result is that we have clarified the morphology of the whole pentacene film excluding the influence of the atmosphere completely.

In order to probe the molecular orientation from a viewpoint of the direction of an electron orbital, we measured the NEXAFS of pentacene films. Fig. 3 shows the C K-edge NEXAFS spectra of pentacene films deposited on the SiO_2 substrate prepared by Shiraki method. Pentacene films deposited on SiO_2 substrates prepared by other methods showed similar NEXAFS spectra. Intense peaks observed around 283–288 eV can be assigned to the transitions from C 1s to π^* orbital (perpendicular to the pentacene molecular plane; π^*-peak) [13,14]. Splitting of the π^*-peak could be attributed to the transitions from C 1s to LUMO and LUMO+1, while the fine structures in