# Nanoscale polydiacetylene wire structures prepared by molecular beam deposition on semiconductor substrates

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## Abstract

Preparation of organic nanostructures was studied by molecular beam deposition of polydiacetylene on GaAs(1 0 0) substrates. We have found that single-crystal wires and sheets with nanometer scale can be prepared by controlling substrate temperature and deposition rate. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Polydiacetylene; Molecular beam deposition; Nanostructures

## 1. Introduction

In view of low-dimensional structures, conjugated polymers would be very interesting if one can intentionally modify the size and shape of wavefunctions of delocalized $\pi$ electrons. In order to perform such modification, methods for the preparation of crystalline thin films and microstructures with atomic precision have to be developed. Analogous to the control of nucleation process in semiconductor heteroepitaxy [1], we believe that the orientation of monomer/polymer units is one of the most important steps to be controlled during the deposition.

This work aims at studying the methods to obtain crystalline polymer films directly on semiconductor substrates. As a model system, we have chosen one of the polydiacetylenes (PDA) derivatives, poly-(5,7-dodecadiyne-1, 12-diyl-bis-butyl-urethane) (Poly-4U$_4$). As shown schematically in Fig. 1a, this polymer consists of [=C–C≡C–C=] main chains and [–(CH$_2$)$_4$–OCONH–(CH$_2$)$_3$CH$_3$] side chains, and is known to be synthesized in the form of PDA polycrystals by photo polymerization [2]. The structure of the crystal is monoclinic (Fig. 1b). Photo-induced change in color has also been reported, and discussed in terms of strong phonon–electron interaction in low-dimensional systems involving polaron formation [3].

We describe, in this paper, the preparation of PDA thin films by molecular beam deposition. We point out that single-crystal wires and sheets with the width and thickness of a few tens of nanometers can be prepared in a large area under the proper growth conditions.

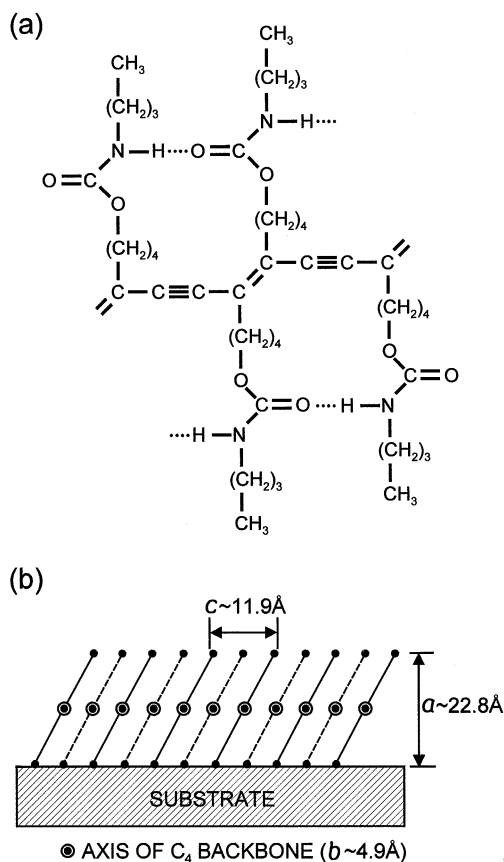* Corresponding author. Fax: + 81 45 924 5175; e-mail: tkondo@isl.titech.ac.jp.

(a)



(b)



◎ AXIS OF $C_4$ BACKBONE ($b \sim 4.9$Å)

Fig. 1. (a) Molecular structure of poly-4U$_4$. Dotted lines show hydrogen bonds, and (b) schematic illustration of a monoclinic poly-4U$_4$ crystal film with three lattice parameters $a$, $b$, and $c$. Values of the parameters are taken from Ref. [4] for the high-temperature (red) phase. PDA planes shown by broken lines are expected to be off by $b/2$ along the $b$-axis with respect to the planes shown by solid lines.

## 2. Experimental

Molecular beam epitaxy machine was used to study the deposition of PDA films on semi-insulating Cr,O-doped GaAs(1 0 0) substrates. The substrates were cleaned by the conventional method using a sulfuric-acid-based solution, loaded into a growth chamber through the load lock system, and were heated at the substrate temperature of $T_s = 580°C$ under an As$_4$ beam flux to remove the surface oxide layer. This was followed by prepara-

tion of a GaAs buffer layer at $T_s = 520°C$ to yield either $(2 \times 1)$ or $(2 \times 4)$ reconstructed flat GaAs surface. This step is very crucial to obtain PDA films with fixed orientation. After the formation of the buffer layer, the substrate temperature was reduced to $T_s = 30–120°C$ for the deposition of PDA. A monomer of PDA–4U$_4$ (DA–4U$_4$) was used as a source material, and was evaporated at the effusion cell temperatures of 58–80°C. This temperature range gives rise to the beam flux intensity of $1.0 \times 10^{-7}–4.0 \times 10^{-7}$ Torr, respectively. During the deposition, substrates were irradiated with 365 nm UV light ($\sim 3$ W/cm$^2$) to promote the photo-induced polymerization. This process results in the enhanced sticking coefficient of source molecules, making it possible to raise $T_s$ higher than the effusion cell temperature.

PDA films were characterized by non-contact mode atomic force microscopy (NC-AFM), X-ray diffraction, and micro-Raman spectroscopy to obtain information as to both macroscopic and microscopic structures. We have made great effort to measure the same area by different methods to extract the correlation between wire axis and the orientation of =C–C≡C–C= backbones. In some cases, experiments were carried out by using PDA samples grown on patterned GaAs(1 0 0) substrates.

## 3. Results and discussion

Systematically studying the preparation of PDA layers under various deposition conditions, we have found three different regions depending on the substrate temperature $T_s$ and the deposition rate $R$. The results are schematically summarized in Fig. 2. The first region (a hatched area in Fig. 2) is defined by the relatively high deposition rate and low substrate temperature, in which nanometer size PDA wire structures can be prepared. Within the limit of this region, overall wire alignment degrades with increasing $R$. The second region (a gray area in Fig. 2) is defined by the relatively low $R$ and high $T_s$, in which the deposition results in the homogeneous layered structures. The third region is defined by high $T_s$ ($> 120°C$) in which the sticking coefficient of a DA–4U$_4$ monomer is virtually zero so that no deposition takes place.
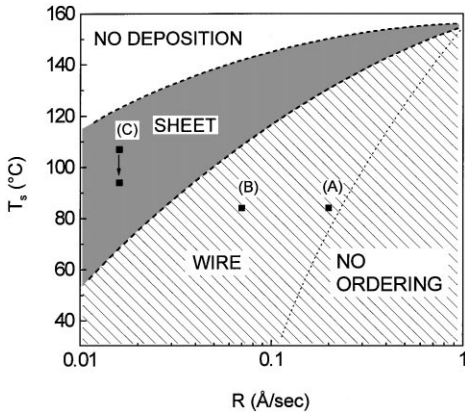
Fig. 2. Schematic diagram of film morphology in connection with substrate temperature $T_s$ and deposition rate $R$. Samples shown in this paper were represented by points A, B, and C.

In Fig. 3, we show a plan view NC-AFM image of a PDA sample (sample A) obtained from the "wire" region. The sample was prepared at $T_s = 85°C$ with $R \sim 0.2$ Å/s. The deposition time was 60 min. The image clearly shows that the sample consists of wires with the width and height of tens of nanometers. Wires primarily align themselves along the same direction within the area of about 5 μm square when deposition is carried out with reduced $R$ ( $\leqslant 0.2$ Å/s) and relatively high $T_s$. As a result of this behavior, surface is covered by domains with different orientations. On the other hand, wires coils themselves round when PDA is deposited with $R > 0.3$ Å/s. We refer this situation to "no ordering" in Fig. 2. As to the growth mechanism, we infer that high density of PDA nuclei is produced under a high beam flux of DA source molecules, which in turn results in the formation of wires. This process may be understood as analogous to the three-dimensional island growth in the epitaxy of semiconductor layers.

In Fig. 4, we are able to see the initial stage of the wire formation. The sample was prepared at $T_s = 85°C$ with $R \sim 0.07$ Å/s (sample B in Fig. 2). PDA wires of height, width, and length of 2 nm, $\sim 40$ nm, and 5–10 μm, respectively, are clearly seen in the figure. It should be noted that the size of domain increases with improving the quality of the GaAs surface. So far, samples with large domain
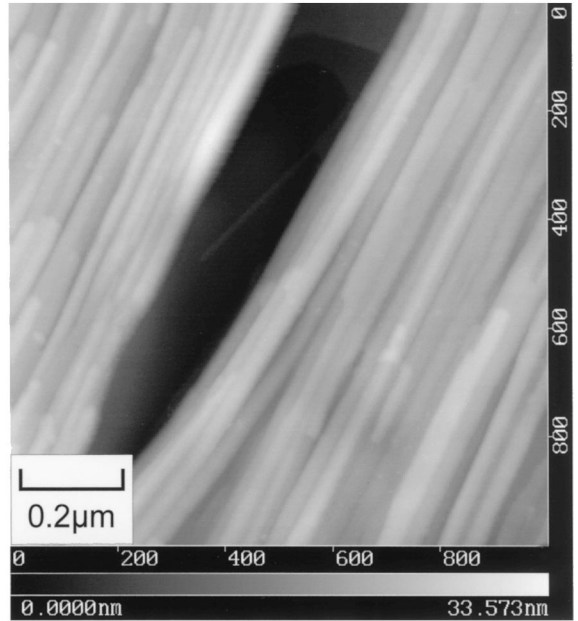


Fig. 3. Plan view NC-AFM image of the PDA film deposited at $T_s = 85°C$ with $R = 0.2$ Å/s (sample A).
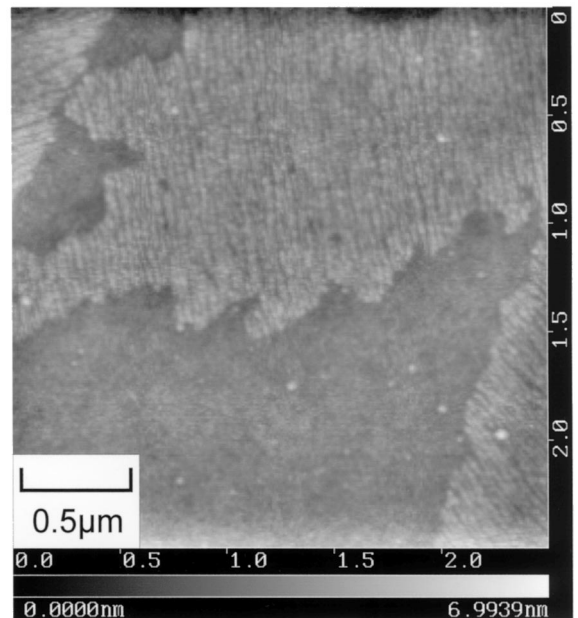


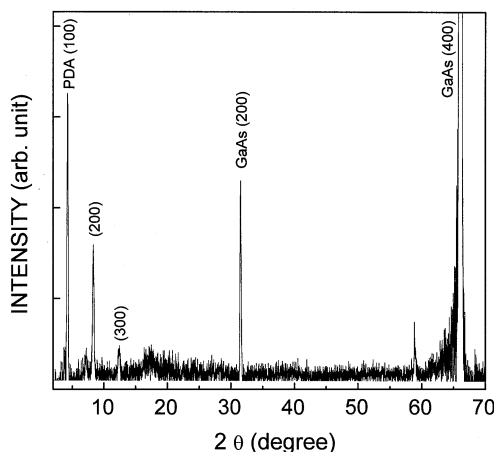Fig. 4. Plan view NC-AFM image of the PDA film deposited at $T_s = 85°C$ with $R = 0.07$ Å/s (sample B).
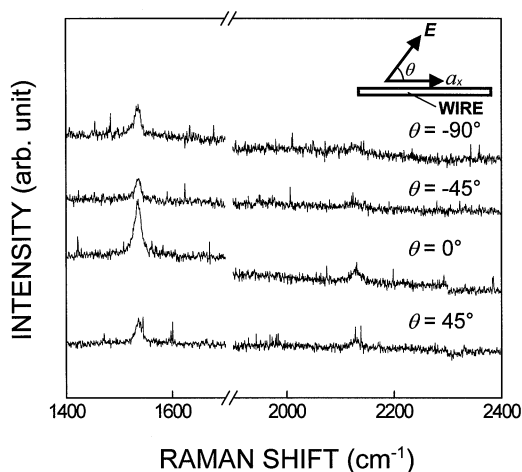
Fig. 5. X-ray diffraction data of sample A.



Fig. 6. Micro-Raman spectra of the sample with wire structures. $\theta$ represents the degree of rotation of polarization plane with respect to the PDA wire axis.

size ($\sim 10\ \mu m$ square) can be prepared when PDA is deposited on $(2 \times 4)$-reconstructed smooth GaAs surface.

Fig. 5 shows X-ray diffraction data of the PDA sample shown in Fig. 3. In addition, to the diffraction peaks from a GaAs substrate, three peaks are observed in the low-angle region, being the first-, second-, and third-order diffraction peaks from the $a$-plane of monoclinic PDA crystal unit (Fig. 1b). The observed result indicates that the longest crystal axis ($a \sim 2$ nm) of PDA primarily align parallel to the $\langle 1\,0\,0 \rangle$ direction of a GaAs(1 0 0) substrate.

Fig. 6 shows micro-Raman spectra of PDA wires. The area of analysis is about $3\ \mu m$ in diameter. Here, $\theta$ represents the degree of rotation of polarization plane with respect to the PDA wire axis. Two peaks are noticeable at 1550 and $2100\ cm^{-1}$ which are, respectively, due to the –C=C– and –C≡C– stretching modes of the "red" PDA phase (the high-temperature phase) [4]. For the –C≡C– mode, the intensity is highest at $\theta = 0°$, and is nearly zero at $\theta = -90°$. This indicates that the direction of the –C≡C– bonds is parallel to the wire axis. As to the –C=C– mode, the $\theta$ dependence is not the same as that for the –C≡C– mode. This behavior can be understood by taking into account the microscopic structure of the $C_4$ main chain (Fig. 1a) in which the –C=C– and –C≡C– bonds are not parallel to each other. In short, the results indicate that the wire axis is parallel to the –C≡C–
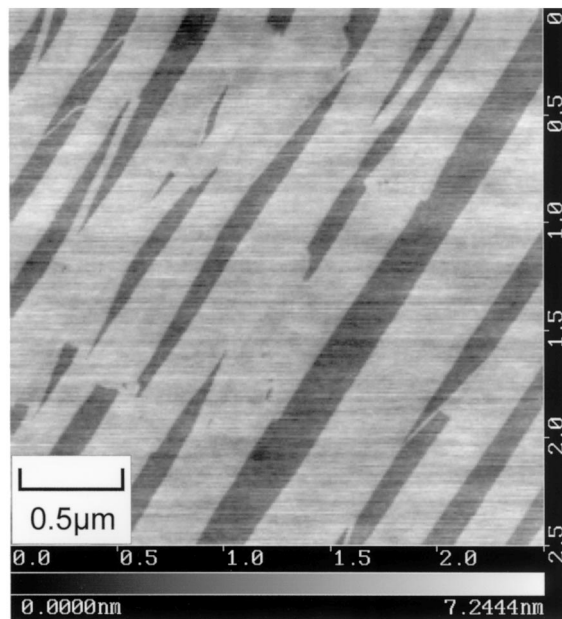


Fig. 7. Plan view NC-AFM image of the PDA film prepared by two-step deposition process (sample C).

bonds, suggesting that the wires are composed of single-crystal phase.

Fig. 7 shows a plan view NC-AFM image of a PDA sample (sample C) obtained from the "sheet"

region. The sample was prepared by two-step deposition process; the first step is for the initial PDA nucleation at $T_s = 107°C$ for 30 min, and the second step is for the normal deposition at $T_s = 94°C$ with $R \sim 0.02$ Å/s. The deposition time of the latter step was 60 min. The surface consists of elongated plateaus whose height is about 2 nm. Note that this value is nearly equal to the spacing of $a$-planes of a monoclinic PDA crystal. On the basis of observed results in the two-step procedure, we infer that small numbers of well-aligned PDA nuclei are formed at the first step, and, at the second step, two-dimensional (2D) growth occurs by utilizing those nuclei. Intriguingly, coalescence of 2D-islands does not result into the formation of gaps in the "sheet" samples, as was the case for the "wire" samples.

It is important to ask whether the quantum size effect can be responsible for modulating the optical and electrical properties of PDA wires and sheets. To pursue further, we are currently measuring photoconductivity of both "wire" and "sheet" samples to investigate the fundamental optical absorption edges.

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