Observation of polyimide monolayers by scanning tunnelling microscopy

T. Hayashi, H. Yamamura and T. Nishi*
Department of Applied Physics, Faculty of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

and M. Kakimoto
Department of Organic and Polymeric Materials, Faculty of Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan
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Monolayers of poly[*N*,*N*′-bis(phenoxyphenyl)pyromellitimide] deposited on highly oriented pyrolytic graphite substrates by the Langmuir–Blodgett technique were successfully observed by scanning tunnelling microscopy.

(Keywords: scanning tunnelling microscopy; polyimide; Langmuir–Blodgett film)

Introduction

Scanning tunnelling microscopy (STM) is a powerful method for observing the surface of materials on an atomic scale. There have been many reports on surface observations of inorganic substances by STM but only a few reports have been published for polymers. Sotobayashi *et al.* reported STM observation of a monolayer of poly[*N*,*N*′-bis(phenoxyphenyl)pyromellitimide] (PI) deposited on highly oriented pyrolytic graphite (HOPG) substrate by the Langmuir–Blodgett (LB) technique[1,2]. They obtained some images with ordered structure from the sample but the detailed structure of the polymer image was not sufficiently clear. The periodicity of the pattern was 1.15 nm along the polymer chain; this was smaller than the molecular dimensions of the most probable conformation of isolated PI chains (1.72 nm). Clearer images of PI thin films on a graphite substrate and a periodicity of ~1.7 nm were obtained by controlling the setting current and the bias voltage for STM.

Experimental

The LB technique[2] was used for sample preparation. The PI monolayer was deposited on an HOPG substrate with a very flat and clean surface. The surface pressure during the film deposition was 5 mN m^{-1}. (This value is lower than that reported in reference 1.) A Nano Scope II (Digital Instrument Inc.) was used for the STM observation.

Results and discussion

Figure 1 shows an STM image of the PI monolayer for a scan area of 2.3 nm × 2.3 nm. *Figure 1a* is an original STM image of the sample. Original images are not clear because of the scanning noise. Further, the STM image of HOPG is overlapped with that of the PI. This is probably due to the low electronic conductivity of the PI monolayer. *Figure 2* shows an STM image of HOPG

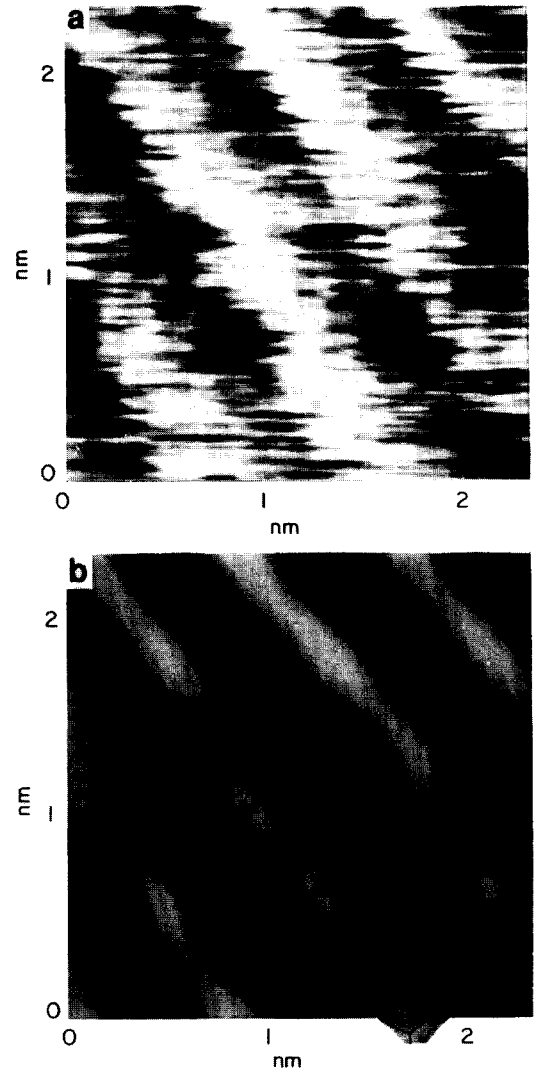

Figure 1 STM image of the PI monolayer for a scan area of 2.3 nm × 2.3 nm: (a) original STM image; (b) filtered image of (a) and a schematic diagram of the PI chain

*To whom correspondence should be addressed

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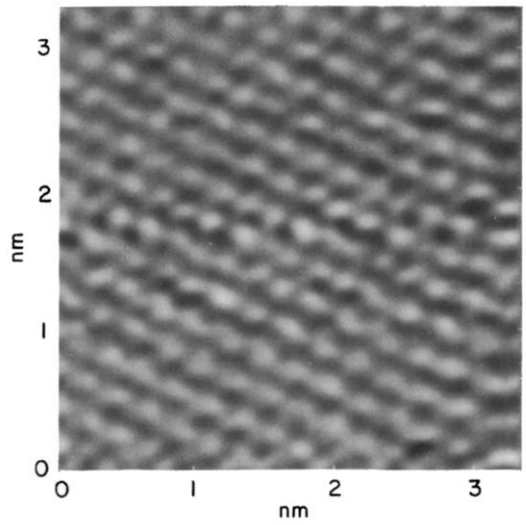

Figure 2 STM image of HOPG from the same substrate as in *Figure 1*

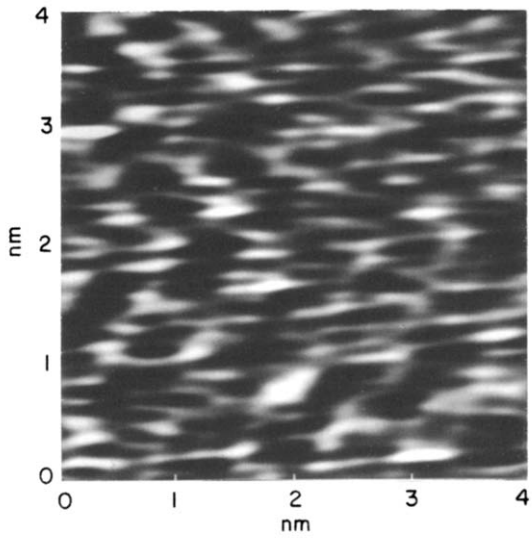

Figure 3 STM image of PI film deposited under a pressure of 20 mN m^{-1}

from the same substrate but with a different bias voltage and setting current. The scanning noise has only high frequency components along the vertical axis of the image. The STM image of HOPG had a very regular hexagonal pattern. On the basis of these observations, a two-dimensional digital frequency filter was used to subtract the scanning noise and the overlapped STM image of the HOPG from the original image. *Figure 1b* shows the filtered image of *Figure 1a* and the molecular structure of the polymer chain is superimposed. From the STM images of the PI monolayer, the repetition pitch along the chain was estimated to be ~1.7 nm along the chain ($P_{\parallel}$) and 0.5 nm perpendicular to the chain ($P_{\perp}$), respectively. These results are consistent with the molecular dimensions of the most probable conformation as can be seen from *Figure 1b*. The angle of the segment of the polymer to the substrate was also estimated. The calculated angle was lower than that given in a previous report[1].

STM images of the PI film deposited at higher surface pressures were also observed. *Figure 3* shows an image of the PI film deposited under a pressure of 20 mN m^{-1}. $P_{\parallel}$ and $P_{\perp}$ in *Figure 3* are the same as in *Figure 1*, though the pressure was higher. The packing density is insensitive to the deposition surface pressure because of a saturation effect.

Clear STM images have been obtained at rather high bias voltages (250–300 mV) and at a very low setting current (~0.1 nA).

The relationship between the STM image and the deposition surface pressure or the number of layers on the substrate will be subsequently reported.

Acknowledgement

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References

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