JOURNAL OF MATERIALS SCIENCE 28 (1993) 1372–1376

Molecular structure and thickness of highly oriented poly(tetrafluoroethylene) films measured by atomic force microscopy

P. DIETZ, P. K. HANSMA, K. J. IHN*, F. MOTAMEDI*, P. SMITH*
*Department of Physics and * Materials Department, University of California, Santa Barbara, CA 93106, USA*

Atomic force microscopy (AFM) was used to image thin single-crystal-like layers of poly(tetrafluoroethylene) (PTFE) deposited mechanically on glass. Not only can AFM reveal details of the molecular structure, but it can also provide direct measurement of the absolute thickness and continuity of these films. High-magnification images show individual rod-like molecules with an intermolecular spacing of 0.58 nm. The helix of individual molecules is clearly resolved and fine structures along the polymer chains may indicate individual fluorine atoms. The thickness of the films varies from 7–32 nm depending on deposition temperature and mechanical pressure. The continuity of the films strongly decreases at lower temperatures. The remaining single fibres are not stable and can be modified by the imaging tip.

1. Introduction

Recently, a new method for producing highly oriented single-crystal-like films of poly(tetrafluoroethylene) (PTFE) was introduced [1]. The simple technique consists of dragging a bar of the polymer at controlled temperature, pressure and speed against a smooth glass substrate. Electron diffraction studies of the PTFE films reveal that the chains of the PTFE macromolecules are oriented parallel to the glass and along the sliding direction [1]. The significance of these PTFE films derives from the fact that other materials grown on their surface from solution, melt or vapour also show a remarkable degree of alignment. Advantages of highly oriented polymers compared with unoriented materials can include significant increases of stiffness, strength or electrical conductivity; possible applications are materials reinforcement or molecular electronics.

Atomic force microscopy (AFM) was invented in 1986 by Binnig *et al.* [2]. A sharp stylus is mounted on a cantilever with a low spring constant. The sample is raster-scanned beneath the stylus. Forces acting between the sample surface and the stylus will deflect the weak cantilever. Measuring the displacement of the tip gives a real three-dimensional topographic representation of the sample surface. AFM can image the original surface of non-conducting materials with nanometre scale resolution in air and even under liquids [3]. Consequently, the sample need not be exposed to high vacuum, high energy beams or special preparation techniques. In the field of thin polymeric films such as PTFE, AFM has the advantage that it can reveal two different kinds of important information. At high resolution it can image the molecular arrangement with single molecule and even submolecular resolution. Simultaneously, a low-resolution measurement can give the absolute height and homogeneity of the films.

AFM investigations of films and crystals of polymers and polymer-related compounds have been recently reported, including molecular resolution images of polyethylene dendrites [4], cold-extruded polyethylene [5], polypropylene [6], cyclic alkanes [7], PTFE and polycarbonate [8]. A previous AFM study of the structure of highly oriented PTFE films [9] showed that the resolution is sufficient to distinguish individual macromolecules. In this paper we present the first direct observation of the helical structure of individual PTFE molecules and report a method to measure the absolute thickness of highly oriented PTFE films which allows study of the influence of the preparation parameters on the thickness and continuity of the films.

2. Experimental procedure

The PTFE layers were imaged with a Nanoscope™ FM from Digital Instruments [10]. A schematic drawing of the imaging principle is given in Fig. 1. A pyramid silicon nitride microtip is mounted on a V-shaped cantilever with low spring constant. The sample, which is attached to a piezoelectric *xyz*-translator, is raster-scanned beneath the tip. The displacement of the tip is measured by sensing the deflection of a laser beam reflected off the back of the cantilever with a two-segment photodiode. A feedback loop keeps the vertical position of the tip constant by moving the surface up and down with the piezoelectric translator (constant force mode).

Low contact forces are necessary to prevent deformations of the sample surfaces. We achieve forces

0022–2461 © *1993 Chapman & Hall*

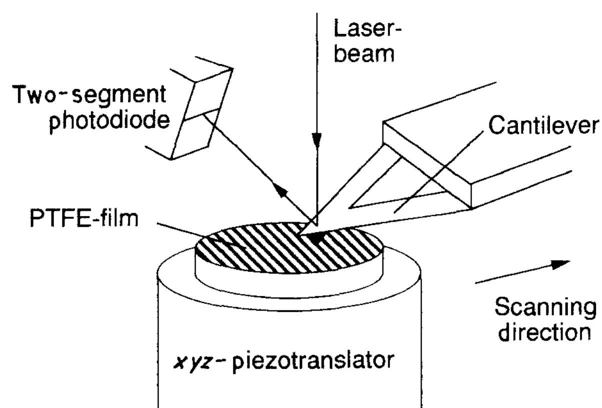


Figure 1 Schematic drawing of the atomic force microscope.

between 10^{-7} and 10^{-8} N by using microfabricated cantilevers with a small spring constant (0.027 Nm^{-1}) [10] and by minimizing the contact force in the force–distance mode of our AFM, as described in detail by Weisenhorn *et al.* [11]. The silicon nitride cantilevers with integrated tips are 200 μm long and 0.6 μm thick. The high-resolution image in Fig. 2 was taken with an "F" scanner, which has a maximum scan range of 8×8 μm^2, the thickness measurements (Figs 3 and 4) were performed with a 120 μm "J" scanner.

Glass microscope slides cleaned in KOH were used as substrates for the PTFE films. A solid PTFE bar was moved along their surface at a rate of 1 mm s^{-1}. In order to study the influence of preparation parameters on thickness and continuity of the films, we varied mechanical pressure and deposition temperature. Films were prepared with pressure between 20 and 40 N cm^{-2} and temperature between 100 and 280 °C; the details are given in Table I. The quality, orientation and continuity of the films were checked in advance by cross-polarized light microscopy. All AFM images were taken in air.

Height measurements of PTFE films could be carried out easily because films prepared at temperatures up to 280 °C do not completely cover the glass substrate. Within scan ranges of 10×10 μm^2, or even smaller, we always found areas where the glass was visible and the height difference between substrate and film could be directly determined from the AFM image. For films with complete coverage, thickness measurements with AFM can still be carried out, e.g. by touching a small soft tool, like a micropipette, to the surface in order to uncover parts of the glass substrate [9]. However, in this case artefacts caused by the damage of the film cannot be ruled out and the height values may be less reliable.

TABLE I Deposition parameters and thicknesses of the highly oriented PTFE films imaged in this study

Film	Temperature (°C)	Pressure (N cm^{-2})	Thickness (nm)
1	100	20	Single fibres
2	200	20	Single fibres
3	230	20	7.3
4	230	40	11.1
5	250	20	8.5
6	250	40	14.0
7	280	20	26.2
8	280	40	32.0

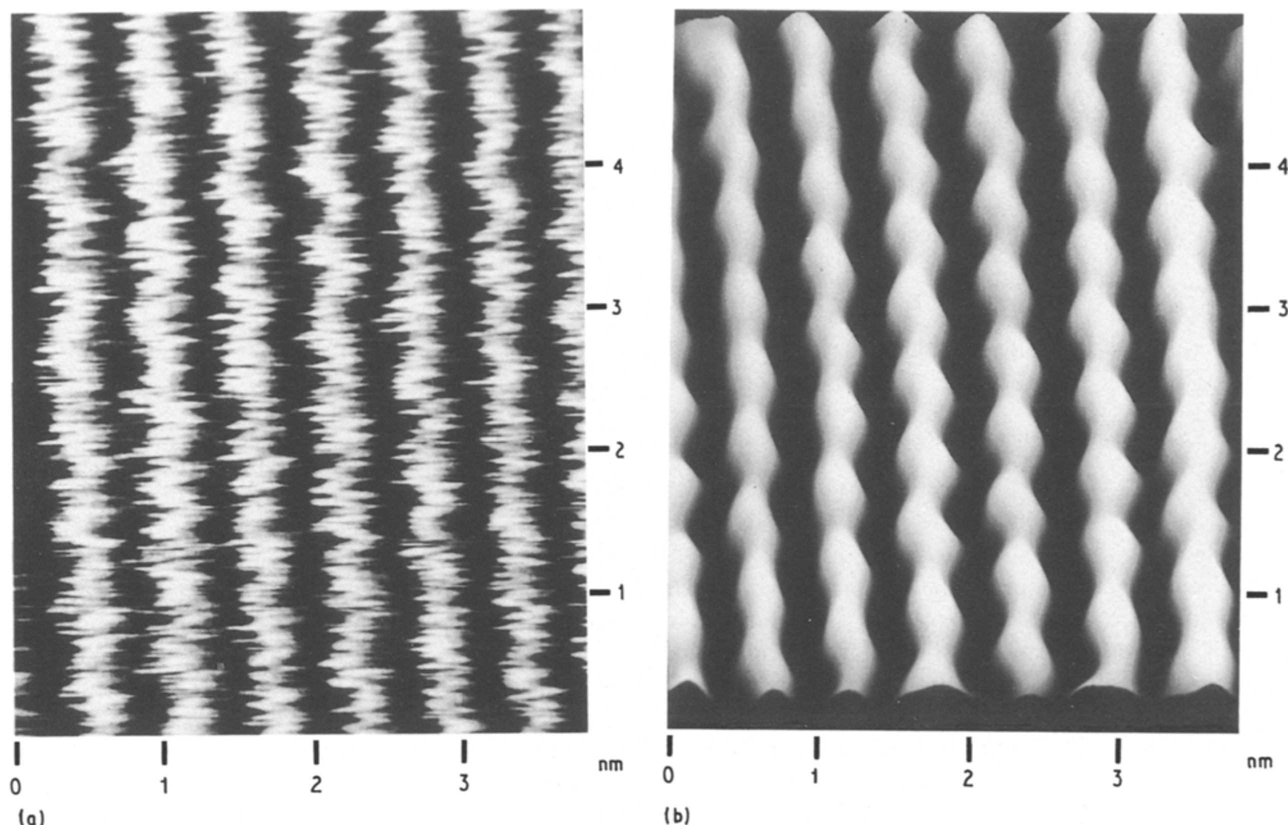
3. Results and discussion

3.1. Molecular structure

A high-resolution AFM picture taken on a highly oriented PTFE-film is shown in Fig. 2. Individual PTFE macromolecules can be readily distinguished, with intermolecular spacings of 0.58 ± 0.06 nm. The AFM was calibrated in *x*- and *y*-directions by imaging the well-known hexagonal structure of mica, which has a lattice spacing of 0.52 nm. Bunn and Howells [12] found from electron diffraction studies that the chain stems of crystalline PTFE molecules are packed on a nearly hexagonal array with distances between single chains of 0.554 nm, which is in good agreement with our result.

In addition, twists in individual molecules are clearly visible in these AFM images. The helical structure can be emphasized by filtering the image in Fourier space, a procedure that smoothes the fine structure along the single twists, and by using a perspective representation with a view angle of 60° (Fig. 2b). The distance between single twists in this image is about 0.57 ± 0.06 nm. What we imaged here is most likely the top layer of the fluorine helix of individual PTFE molecules. The fine structure along the twists which can be seen in the unfiltered image (Fig. 2a) is presumably produced by individual fluorine chain atoms. Molecule cross-sections indicate that in some areas three or four individual fluorine atoms within one elevation of the molecule can be counted. Earlier AFM observations on SrF_2 single-crystal surfaces confirm that the AFM is able to resolve individual fluorine atoms [13].

Comparison of our image with a model of the PTFE molecule that was derived for electron diffraction observations [12] (Fig. 2c) shows qualitatively good agreement. In this model, which was based on a PTFE layer prepared below 20 °C, a full 360° twist of the chain occurs in 3.36 nm, 13 zigzags or 26 chain atoms, but the actual period is half this, because a zigzag consists of two lines of atoms, and a half twist brings the fourteenth atom on the second line directly above the first atom on the first line. Taking into account that the elevations of the fluorine helix are observed in our AFM images, we would find four of these elevations within 3.36 nm (see model in Fig. 2c) resulting in a periodicity of 0.84 nm along the chains. The period measured from Fig. 2 is 0.57 ± 0.06 nm, which is about 30% below the expected value. Because the accuracy of the *x*- and *y*-calibration of the microscope, derived from mica observations, is generally better than ± 10%, we conclude that the special film processing technique which is used here may have produced a different PTFE configuration with an increase of the chain period. Changes in the structure of PTFE at certain transition temperatures, including increase of chain period, have been reported by others [12, 14].



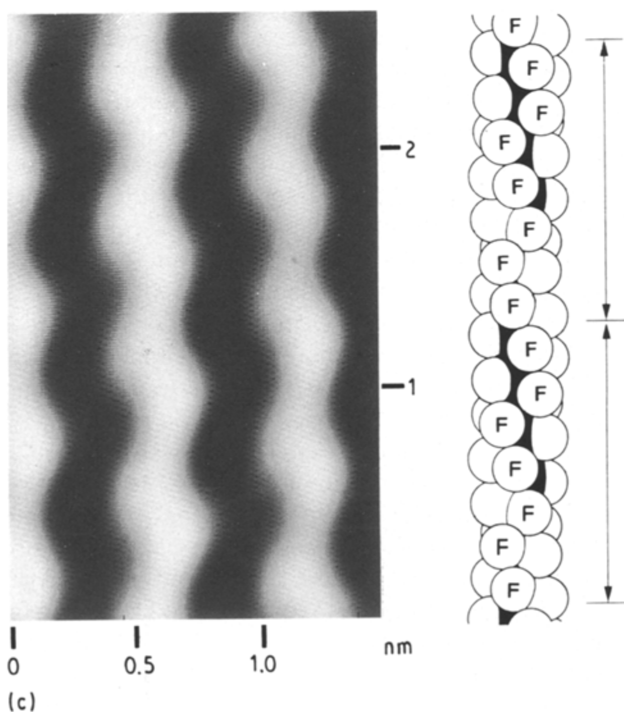
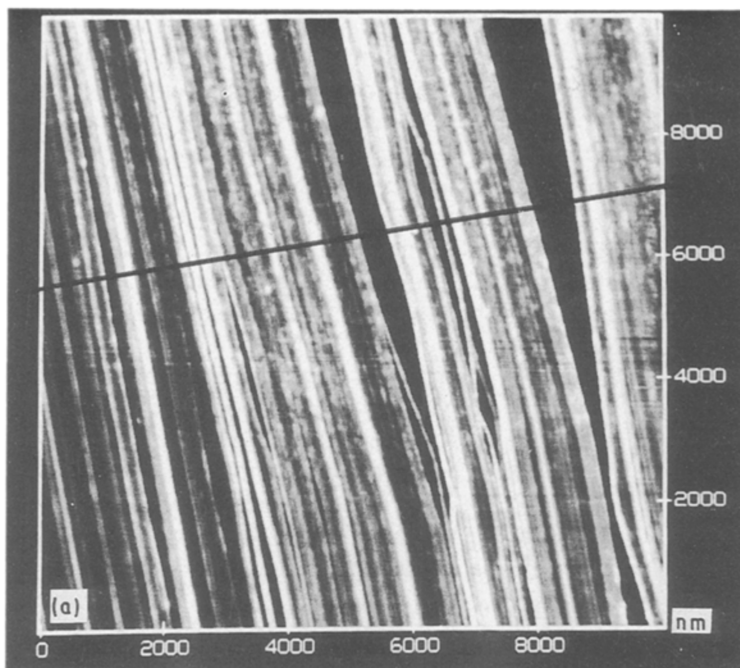


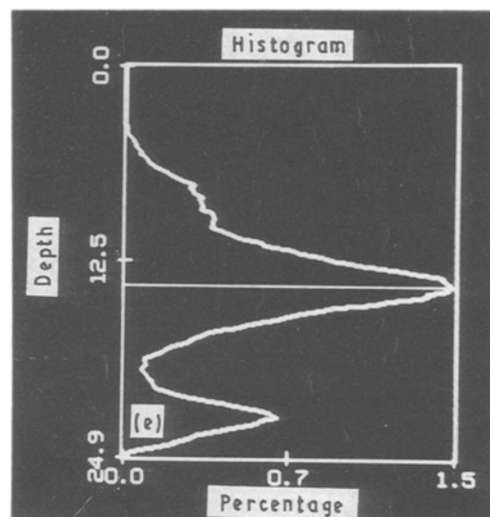
Figure 2 AFM image of individual molecules on a highly oriented poly(tetrafluoroethylene) (PTFE) film. Deposition parameters: $P = 40\ \mathrm{N\ cm^{-2}}$, $T = 300\,^{\circ}\mathrm{C}$. (a) Raw image. Image size is $3.8 \times 5.0\ \mathrm{nm^2}$, scanning rate was 26 Hz. Note the fine structure along the molecules, which is probably produced by individual fluorine atoms. (b) Same image after Fourier filtering. The perspective representation emphasizes the helical character of the molecules. (c) Comparison between AFM image and a PTFE model derived from electron diffraction studies [12]. The arrows indicate the chain repeat distance. Note how the right molecule in the AFM image resembles the model.

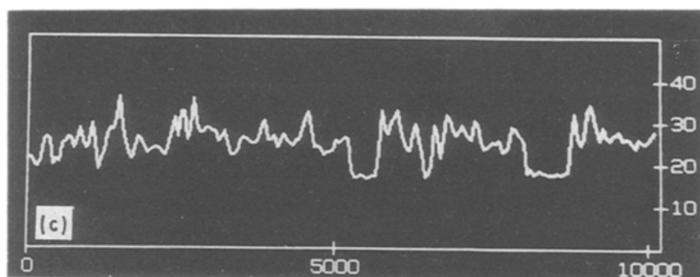
3.2. Thickness and continuity

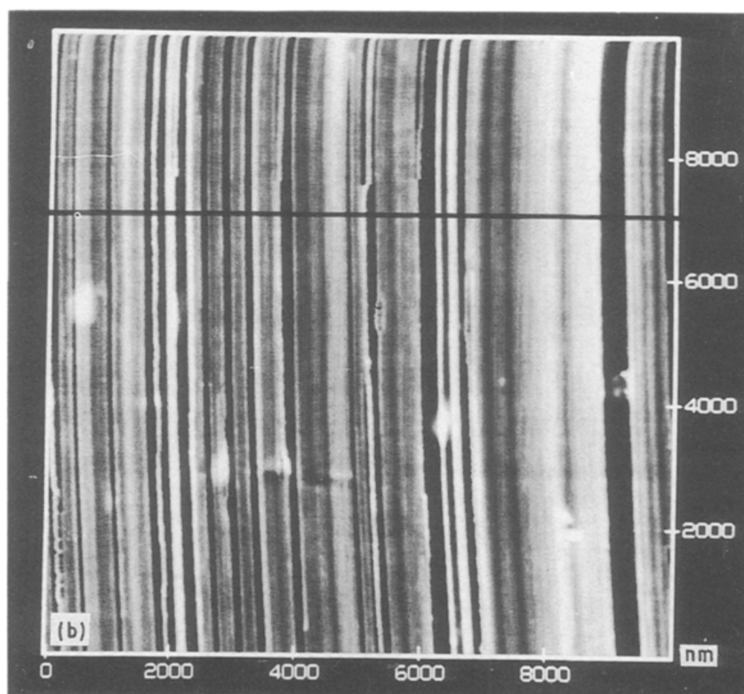
Micrometre-scale AFM images were used to measure smoothness and thickness of eight PTFE films grown under different deposition conditions (Table I). We found that the most influencial parameter is the temperature. Films deposited between 230 and 280 °C show typical row-like structures which cover the glass surface almost completely. However, 5%–20% of the glass is still visible between these PTFE rows, a fact that can be utilized for the height measurements. Two typical examples of films deposited in this temperature range are given in Fig. 3. The cross-sections at the bottom of each picture which were taken perpendicular to the rows, illustrate that the height of the films is not homogeneous but spreads over a wide range up to tens of nanometres. For example, the film in Fig. 3a, which was deposited at 230 °C and with $20\ \mathrm{N\ cm^{-2}}$, has an average height of only 8.5 nm but shows height variations up to 15 nm. The uncovered parts of the glass substrate are clearly visible in the picture as well as in the cross-section.

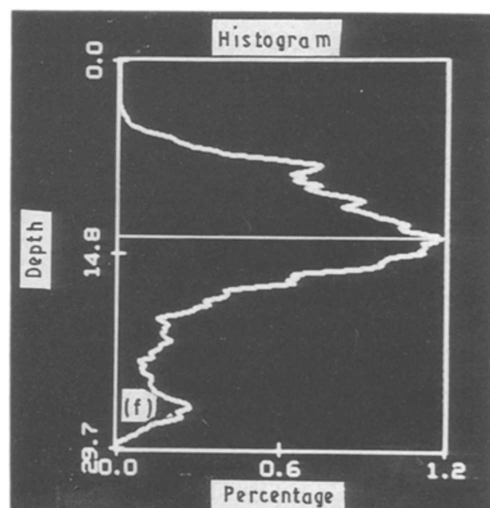
Height distribution curves which can be calculated from the AFM images are excellent both to characterize the homogeneity of the films and to determine the thickness. Generally, two peaks are clearly visible in the distribution curves (see Fig. 3) of our films, one corresponding to the PTFE layer, the other to the glass substrate. The difference between the mean value of the film height distribution and the mean value of the glass height distribution (the glass substrate is not flat on the atomic scale) gives the average thickness of the film. In addition, the width and shape of the height distribution curve contain information on homogeneity and smoothness of the film.











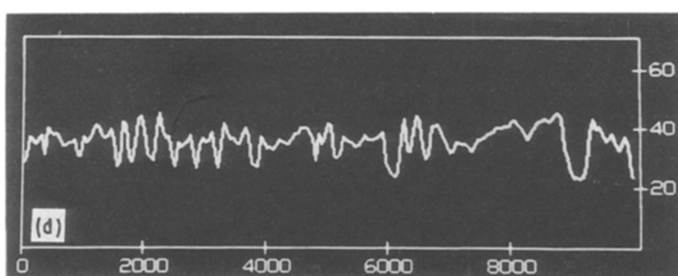


Figure 3 Micrometre-scale AFM images of highly oriented PTFE films deposited under different conditions: (a) $P = 20\ \mathrm{N\,cm^{-2}}$, $T = 230\,^{\circ}\mathrm{C}$, (b) $P = 40\ \mathrm{N\,cm^{-2}}$, $T = 250\,^{\circ}\mathrm{C}$. Image size is $10 \times 10\ \mu\mathrm{m}^2$, scanning rate was 4.4 Hz. Note the PTFE rows running in the direction in which the polymer was laid down. (c, d) Cross-sections perpendicular to the orientation of the films. (e, f) Height distribution curves used to determine the average film height.

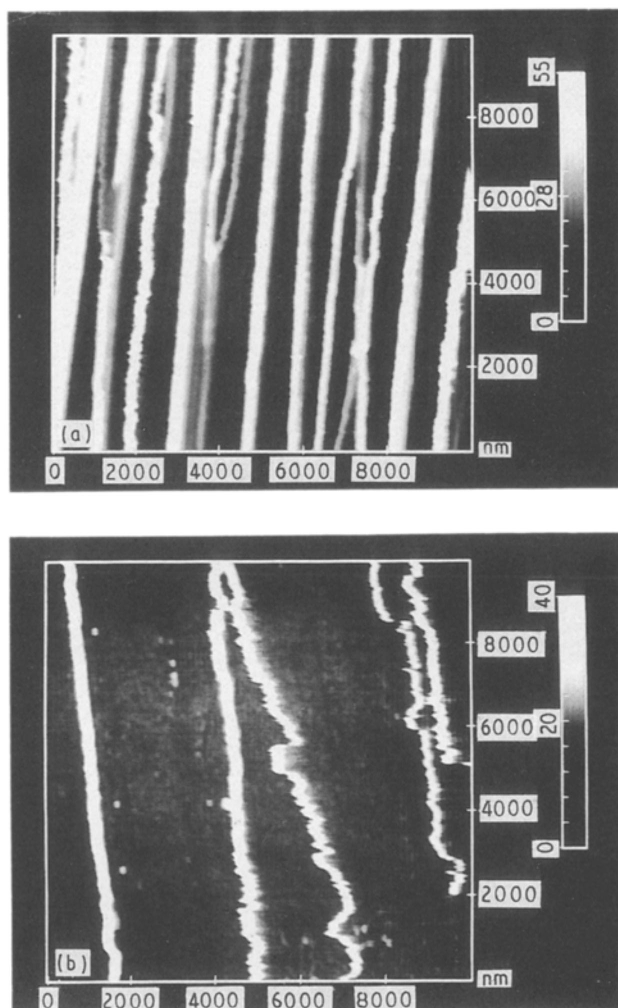


Figure 4 PTFE films grown at lower temperatures. (a) 200 °C, (b) 100 °C. Pressure and scanning parameters as in Fig. 3a. Note the dissection and displacement of single fibres by the AFM tip.

Thickness values for the films in Fig. 3 and for four other films are given in Table I ranging from 7–32 nm. As expected, the thickness increases both with increasing temperature and with increasing mechanical pressure. X-ray data of the films [15] show the same tendency as our results. But in contrast to the AFM, X-ray measurements can only reveal relative values of the film thickness.

At deposition temperatures below 200 °C the quality of the films deteriorates significantly. Less than 50% of the glass surface is covered by a film deposited at 200 °C (Fig. 4a) and less than 10% by a film grown at 100 °C (Fig. 4b). The films disintegrate into single fibres with diameters of about 300 nm. The stability of these fibres is not as high as in the closer packed films, and interactions between the imaging tip and these fibres were frequently observed. Parts of the fibres were dissected and displaced resulting in zigzag structures along the fibres as seen in Fig. 4b.

4. Conclusions

Atomic force microscopy as a new high-resolution technique that provides direct three-dimensional information of the original unprepared sample surface, has become an invaluable companion to electron microscopy in the field of materials research. We have shown that AFM can be useful for the characterization of highly oriented PTFE films on a scale from tens of micrometres to less than 1 nm. The microscope is able to resolve details of the molecular structure, such as the fluorine helix, with submolecular resolution and at the same time, can provide detailed information on the absolute film thickness and the homogeneity of the films. The latter information will be especially important in developing an understanding of the orienting faculty and in improving the quality of the layers in dependence upon the deposition conditions. Highly oriented PTFE films show a remarkable capability to orient a wide variety of other molecules. Promising AFM applications for the near future might be the characterization of such systems.

Acknowledgements

We thank H. Hansma for sharing her AFM experience on PTFE films. This project was supported by the Deutsche Forschungsgemeinschaft fellowship Di 440/1-2 (P.D.), the National Science Foundation, Solid State Grant DMR89-17164 (P.K.H.) and the Office of Naval Research (P.K.H.).

References

1. J. C. WITTMANN and P. SMITH, *Nature* **352** (1991) 414.
2. G. BINNIG, C. F. QUATE and CH. GERBER, *Phys. Rev. Lett.* **12** (1986) 930.
3. D. RUGAR and P. K. HANSMA, *Phys. Today* **43** October (1990) 23.
4. R. PATIL, S. J. KIM, E. SMITH, D. H. RENEKER, and A. L. WEISENHORN, *Polym. Commun.* **31** (1990) 455.
5. S. N. MAGONOV, K. QVARNSTROM, V. ELINGS and H. -J. CANTOW, *Polym. Bull.* **25** (1991) 689.
6. B. LOTZ, J. C. WITTMANN, W. STOCKER, S. N. MAGONOV and H. -J. CANTOW, *ibid.* **26** (1991) 209.
7. W. STOCKER, G. BAR, M. KUNZ, M. MOLLER, S. N. MAGONOV and H. -J. CANTOW, *ibid.* **26** (1991) 215.
8. S. N. MAGONOV, S. KEMPF, M. KIMMIG and H. -J. CANTOW, *ibid.* **26** (1991) 715.
9. H. HANSMA, F. MOTAMEDI, J. C. WITTMANN, P. SMITH and P. K. HANSMA, *Polym. Commun.* (1992) **11** (1992) 41.
10. T. R. ALBRECHT and C. F. QUATE, *J. Vac. Sci. Technol.* **A 6** (1988) 271.
11. A. L. WEISENHORN, P. K. HANSMA, T. R. ALBRECHT and C. F. QUATE, *Appl. Phys. Lett.* **54** (1989) 2651.
12. C. W. BUNN and E. R. HOWELLS, *Nature* **18** (1954) 549.
13. P. DIETZ, C. A. RAMOS and P. K. HANSMA, *J. Vac. Sci. Technol. B* **10** (1992) 741.
14. J. F. WHITNEY, R. H. PIERCE and W. M. D. BRYANT, Abstracts of the American Chemical Society Meeting (March 1953).
15. P. SMITH, unpublished X-ray results, Materials Department, University of California, Santa Barbara.

Received 17 March
and accepted 6 July 1992