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Epitaxial and graphoepitaxial growth of materials on highly orientated PTFE substrates

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The mechanism by which friction-deposited, highly orientated poly(tetrafluoroethylene) (PTFE) films promote orientated growth of materials was investigated. For this purpose, transmission electron microscopy was used to determine the orientation of polyethylene and 1,4-bis-2-(5-phenyloxazolyl)benzene (POPOP) crystals grown from the vapour phase onto the single crystal like PTFE films. Electron diffraction patterns revealed that the polyethylene crystals adopted an orientation that minimized the lattice mismatch at the interface between this material and the PTFE substrate. On the other hand, the POPOP crystals aligned in a fibre pattern, implying that orientated growth occurred because of the grating-shaped surface topography of the PTFE films. Evidently, the latter films were capable of promoting orientated growth of materials by a graphoepitaxial mechanism or conventional epitaxy, depending on the material used.

1. Introduction

The term epitaxy generally refers to the orientated growth of one crystal upon another, the lattice orientation of the growing material being determined by that of the substrate [1]. It is well established that the surface topography of a crystalline or amorphous substrate also can influence the orientation of the growing material, a process known as graphoepitaxy [2] or diataxy [3]. For example, microscopic gratings in amorphous substrates have been observed to orientate KCl, liquid crystals, and various metals [2]. In addition, metal islands crystallized on the surfaces of cleaved alkali halides have been observed to be graphoepitaxially orientated with respect to cleavage steps [4].

Recently, it was shown [5] that a variety of materials exhibit highly orientated growth on aligned poly (tetrafluoroethylene) (PTFE) thin films, which were produced by friction transfer of the polymer onto smooth, rigid substrates, as originally discussed by Tabor and coworkers [6, 7]. The polymer chains of these films are aligned parallel to the substrate surface and along the deposition direction. It was demonstrated [5] that these PTFE coated substrates are very effective at promoting orientated growth of a wide selection of materials, including polymers, liquid crystals and small organic and inorganic molecules, deposited onto them from the melt, solution, or vapour phases. It was suggested that the remarkable orientation-inducing ability of these films is due mainly to the presence of small-scale steps or grooves at their surfaces, in addition to the presence of crystalline order perpendicular to the PTFE chain axis; at temperatures above 19 °C, where orientated growth is generally carried out, the PTFE crystal structure largely lacks order along the chain axis [8, 9].

Several studies have addressed the structure of these friction deposited PTFE films at room temperature [10–12], where PTFE is in the hexagonal phase IV [13]. The polymer chains of the film are arranged in a single crystal-like pattern, with a close packed plane parallel to the substrate upon which the film is deposited [10]. Atomic force microscope (AFM) measurements have shown that the surface topography of the film consists of small scale grooves running along the PTFE chain direction [11, 12].

A recent study appeared to present convincing evidence of orientated growth on PTFE films by a conventional epitaxial mechanism [14]. Yang *et al.* [14] found that dimethyloligothiophenes orientated on PTFE films with the a-axis of the oligomers (length = 0.598 nm) parallel to the interchain (a or b) axis of PTFE (length = 0.566 nm), thus minimizing the lattice mismatch between the two materials. On the other hand, Frey *et al.* [15] argued that epitaxy was not a likely cause of the orientation of poly(di-n-alkyl-silylenes) observed to occur on PTFE substrates, "given the different molecular geometries and cell parameters of PTFE and the polysilylenes", and suggested that "grooves on the PTFE surface may (induce) anisotropic nucleation" of these materials.

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In the present study, the hypothesis was tested that highly orientated PTFE films can orientate materials by a graphoepitaxial mechanism. To accomplish this task, the lattice orientation of two materials, polyethylene and 1,4-bis-2-(5-phenyloxazolyl)benzene or "POPOP" ($C_{24}H_{16}N_2O_2$), crystallized on such films, was determined. If conventional epitaxy was the dominant orientation mechanism, the crystallizing material should (typically) orientate according to a lattice matching criterion, like the aforementioned oligothiophenes. If graphoepitaxy were the dominant mechanism, on the other hand, the crystallizing material would simply adopt an orientation that maximizes the crystal–PTFE contact area. Thus, molecules or nuclei with large aspect ratios would be expected to align parallel to steps or grooves on the PTFE film in a fibre-like orientation. Of course, both mechanisms could operate in conjunction, i.e. the grooves promoting orientated nucleation of materials and allowing for lattice matching normal to the PTFE chain direction.

2. Experimental procedure

PTFE films were produced by sliding a bar of commercial grade PTFE on cleaned glass slides at a temperature of 300 °C, a contact pressure of 1 MPa, and a sliding rate of 1 mm s^{-1}. Details of the friction deposition method used are discussed in previous publications [10, 16].

AFM was used to reveal the topography of PTFE films at the submicrometre level. Previous studies focused on larger scale and atomic scale measurements [11, 12]. In this study, measurements were performed with a Si tip, which had a radius of curvature of ~10 nm, using the "tapping mode" method of the Nanoscope III instrument (Digital Instruments, Santa Barbara, CA).

Crystals of POPOP (supplied by Lambda Physik, Acton, MA) and low molecular weight, linear polyethylene (molecular weight = 2000 kg kmol^{-1}, Polysciences) were grown on the PTFE films from the vapour phase in a bell jar evacuation chamber. The POPOP was allowed to sublime at ~200 °C, while the PTFE coated glass slides were maintained at a temperature of 130 °C in order to optimize the alignment of the POPOP crystals. The polyethylene, which was rapidly heated, precipitated on the films at room temperature.

The crystallographic orientation of the polyethylene and POPOP crystals was determined by transmission electron microscopy (TEM). For this purpose, the samples were coated with carbon and subsequently detached from the glass substrates by a previously described method [10].

3. Results and discussion

AFM images showed that the surface of the PTFE films consisted of grooves or "ridges" and "valleys" (see Fig. 1). Typically, the distance between ridges ranged from 25 to 500 nm, and the height of individual ridges ranged from ~1 to 50 nm. Steps or grooves undoubtedly were present at the atomic scale as well, since more than one crystallographic plane must have been exposed at the sloped surfaces of the films. In addition, there were frequent gaps in the films, running along the polymer chain direction, which contributed to the grating like nature of the topography. The average thickness of the films was ~20–30 nm.

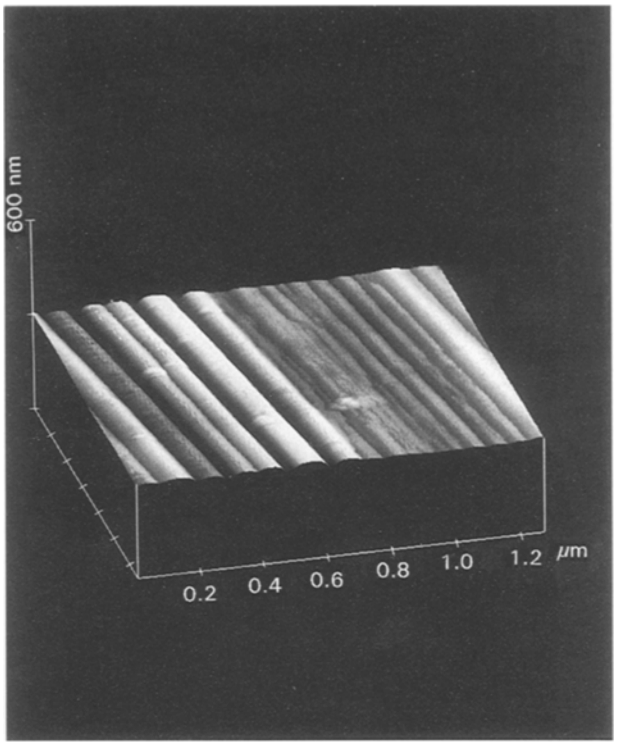

Figure 1 Atomic force microscope (AFM) image of the surface of a friction deposited PTFE film.

Electron diffraction patterns of polyethylene-coated PTFE films revealed that the polyethylene was in the equilibrium orthorhombic phase with the chain axis (*c*-axis) parallel to that of PTFE. When the electron beam was normal to the plane of the film, strong 0 2 0 and 0 1 1 reflections were detected (see Fig. 2a), indicating that the *b*–*c* plane of many of the polyethylene crystallites was parallel to the plane of the sample, or a close-packed plane of PTFE. When the sample was tilted in the electron microscope about the polyethylene–PTFE chain axis, strong 1 1 0 and 2 0 0 reflections were detected (Fig. 2b). The intensity of the 2 0 0 reflection was greatest at a tilt angle of ~30°, whereas the 1 1 0 reflection was most intense at tilt angles of ~25–35°. These observations confirmed that the *b*–*c* planes of the polyethylene crystallites were parallel to the close packed planes of PTFE (see Fig. 3). At this interface, the fractional difference between the interchain distance of polyethylene (0.494 nm) and that of PTFE (0.566 nm) was 12%, the smallest value possible for orthorhombic polyethylene deposited on hexagonal PTFE.

The results of other studies [17, 18] of polyethylene epitaxy suggest that this material could have deposited on PTFE in the metastable monoclinic form, in which the interchain distance in the $(\bar{2}\,1\,0)$ plane is 0.524 nm, and transformed to the orthorhombic form when a critical thickness was reached, leaving a thin

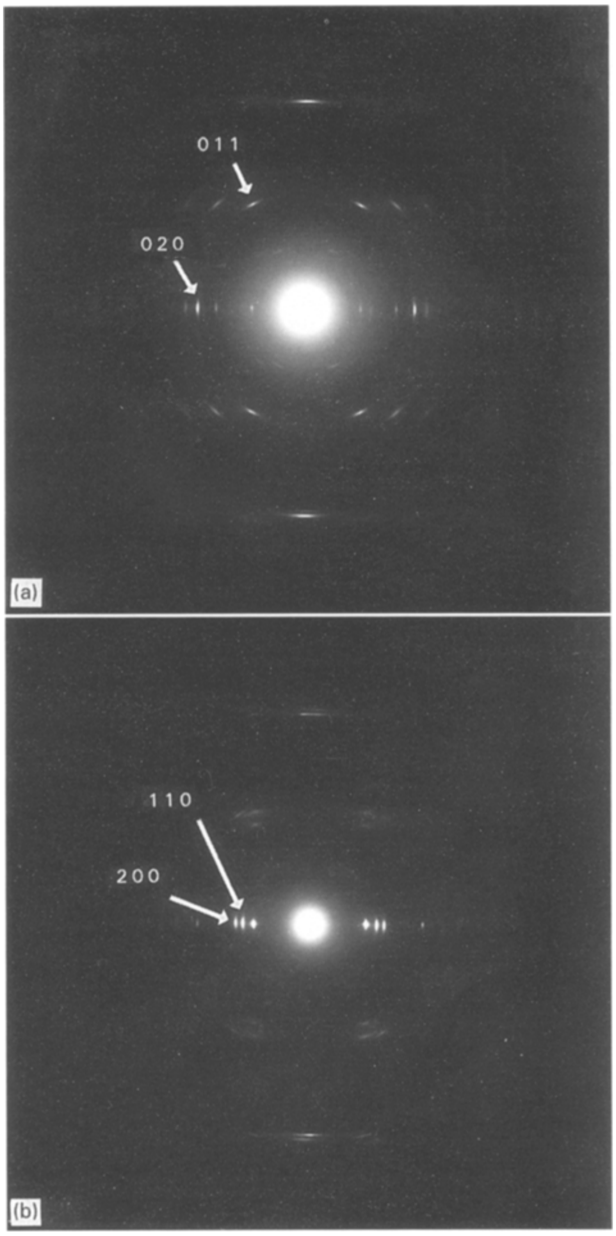

Figure 2 Electron diffraction patterns of polyethylene, crystallized on a highly orientated PTFE film, obtained at tilt angles of (a) 0° and (b) 30° about the PTFE–polyethylene *c*-axis. Reflections from both the polyethylene and PTFE layers are visible. Several of the polyethylene reflections are labelled.

layer (several nanometers) of monoclinic polyethylene between the orthorhombic and PTFE layers. This transformation would have resulted in a 10° rotation of the (1 0 0) plane of the orthorhombic phase from the PTFE–polyethylene contact plane [18]. According to the electron diffraction results, no such rotation occurred. In addition, no reflections from the monoclinic phase, e.g. $1\,1\,1_m$ reflections were detected, although the PTFE and orthorhombic polyethylene layers would have been thicker than the monoclinic layer. Thus, in the present study, polyethylene appeared to nucleate epitaxially on PTFE films in its stable orthorhombic form.

POPOP crystallized on the PTFE films in the form of long needles aligned parallel to the PTFE chain (or groove) direction, as shown in Fig. 4. Electron diffraction patterns, e.g. Fig. 5, revealed that POPOP was

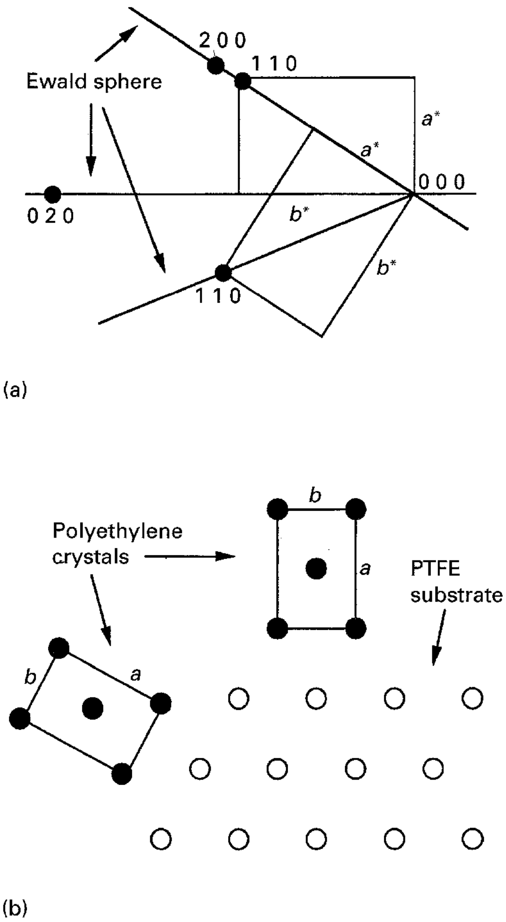

Figure 3 (a) The distribution of structure factors of polyethylene crystallized on PTFE films, and (b) the corresponding arrangement of the polyethylene crystals on the PTFE substrates. The *c*-axis of both materials is normal to the plane of the figure.

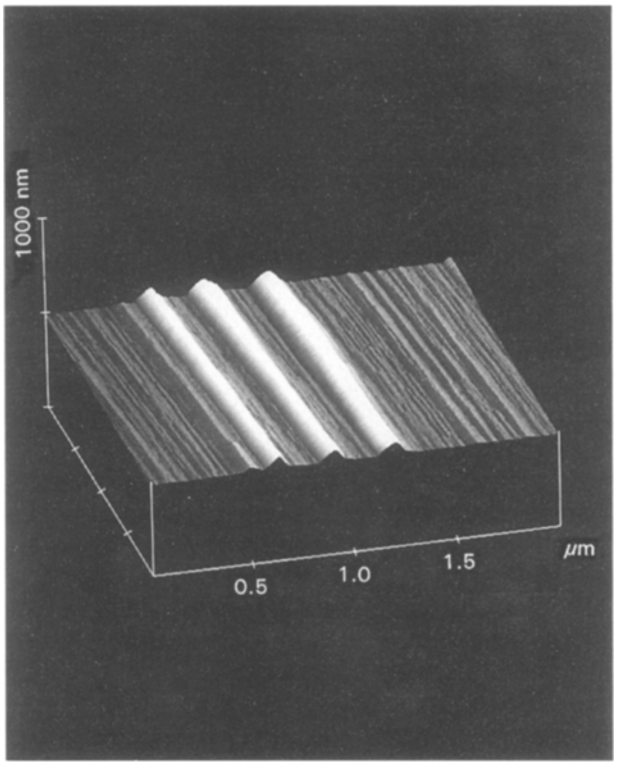

Figure 4 AFM image of needle-shaped crystals of POPOP aligned parallel to the grooves on a PTFE film.

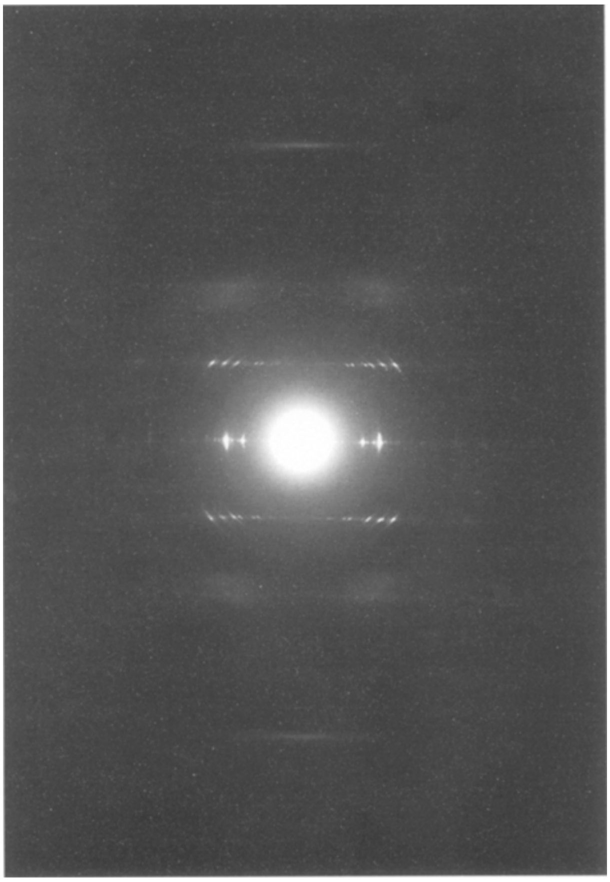

Figure 5 Electron diffraction pattern of POPOP crystals aligned on a PTFE substrate. The POPOP *b*-axis and PTFE *c*-axis are parallel to the meridional in the pattern.

in its equilibrium monoclinic phase ($a = 0.923$ nm, $b = 0.529$ nm, $c = 1.932$ nm, $\beta = 92.09°$) with the *b*-axis parallel to the needle axis [19]. The crystal structure of POPOP, which is illustrated in a previous publication [19], consists of molecules arranged in a crisscrossed pattern. When the sample was rotated about the POPOP *b*-axis (or PTFE *c*-axis), no significant change in the intensity of the POPOP reflections was detected; the crystals were orientated in a fibre pattern. This implies that orientation occurred by a graphoepitaxial mechanism, as discussed above. Evidently, if the POPOP crystals were aligned by a conventional epitaxial mechanism, the *a*- and *c*-axes should have adopted a preferred orientation. In fact, epitaxy probably would have brought the POPOP *b*-axis ($b = 0.529$ nm) parallel to the PTFE *a*- or *b*-axis (0.566 nm), i.e. the POPOP needle axis perpendicular to the PTFE chain axis, rather than parallel to the chain axis as was observed.

4. Conclusions

The results discussed above strongly suggest that the alignment of materials of PTFE films can occur by a graphoepitaxial or conventional epitaxial mechanism, depending on the material used. In some cases, the two mechanisms may operate in conjunction. Whether or not this is true in the case of polyethylene is unclear, but since vapour deposited polyethylene can readily orientate on single crystal substrates [18], this material probably would have been highly orientated on the PTFE films even if their surfaces were completely flat. It is likely that both the lattice structure and the surface topography of the PTFE films promote the alignment of liquid crystals, since single crystal substrates as well as amorphous gratings are capable of orientating such materials [2, 20].

Acknowledgements

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