

Molecular epitaxy of perfluoroicosane on PTFE tribological transfer films studied by XPS and RAIRS

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The molecular orientation of perfluoroicosane (PFI), $n\text{-C}_{20}\text{F}_{42}$, vacuum-deposited onto plain substrates (silicon and gold) and onto poly(tetrafluoroethylene) (PTFE) tribological transfer films, has been studied by angle-dependent X-ray photoelectron spectroscopy (XPS) and reflection-absorption IR spectroscopy (RAIRS). On the plain substrates PFI forms an ordered film with the molecular chains oriented perpendicular to the substrate. However, when deposited onto a PTFE tribological transfer film, epitaxial growth occurs such that the PFI chains align with the PTFE chains, parallel to the substrate. For PFI on silicon, XPS reveals a surface chemical shift for the uppermost CF_3 groups of the sample.

Tribological transfer films of poly(tetrafluoroethylene) (PTFE) were first studied in the 1960s and 1970s,^{1,2} but their ability to induce epitaxy effects in deposited overlayers has been recognised only recently.³ The films are formed when PTFE is drawn, under load, across a smooth substrate at temperatures below the polymer melting point (327 °C). Several techniques have been used to characterise PTFE tribological transfer films, including X-ray photoelectron spectroscopy (XPS),⁴ Fourier-transform IR spectroscopy (FTIR),^{5,6} near-edge X-ray absorption fine structure (NEXAFS),⁷ electron microscopy^{1,2} and atomic force microscopy (AFM).⁸⁻¹⁰ The films consist of PTFE ribbons, typically 200–1000 nm wide by 5–10 nm high and many hundreds of micrometres long, aligned with the film-draw direction and separated by channels of bare substrate. The thickness of the ribbons and the coverage of the substrate increases with deposition temperature and load.⁴ Within the ribbons the helical PTFE chains are also aligned with the draw direction.^{4,7-10}

A wide range of materials, including small organic molecules and polymers, form ordered overlayers when deposited onto PTFE transfer films.^{3,11-21} Deposition techniques include from the vapour phase, from the melt and from solution.³ This is an example of the general phenomenon of polymer on polymer epitaxy,²² which is thought to arise from a combination of classical epitaxy, *i.e.* the matching of specific crystal lattice parameters in the substrate with those in the overlayer, and graphoepitaxy, molecular alignment in the overlayer induced by the gross aligned morphology of the substrate. Polymer on polymer epitaxy already has technological applications in the field of liquid crystal displays and future applications may include the molecular alignment of conducting polymer films for electronic devices. Several publications describe the oriented growth of conducting polymer films on a PTFE transfer film.^{3,13-15}

Linear oligomers of PTFE, $\text{C}_n\text{F}_{2n+2}$, are known to form ordered overlayers on PTFE transfer films³ but details of molecular orientation in the overlayers have not been reported. The deposition of perfluorotetracosane, $n\text{-C}_{24}\text{F}_{50}$, onto copper and rubbed low molecular mass PTFE has been investigated by NEXAFS.²³ This shows that on copper the $n\text{-C}_{24}\text{F}_{50}$ molecular chains orient perpendicular to the substrate whereas on rubbed PTFE they align parallel with the PTFE surface.

In its 'natural' state, perfluoroicosane (PFI), $n\text{-C}_{20}\text{F}_{42}$, forms lamellar crystals with stacked layers of helical molecular chains. Within each layer the molecules are arranged on a hexagonal lattice with their long axes perpendicular to the plane of the layer.²⁴ When vapour deposited onto a plain substrate, PFI orients with the molecular chains perpendicular to the

substrate.²⁵ However, because the crystal lattice parameters and helix pitch of PFI and PTFE are very closely matched,^{24,26,27} epitaxial growth of PFI on a PTFE transfer film might be expected to occur such that the PFI chains align parallel with the substrate. Here we present angle-resolved XPS and reflection-absorption IR spectroscopy (RAIRS) data which clearly demonstrate that this is the case.

Experimental

PTFE tribological transfer films were prepared by drawing a PTFE blade, under load, across a heated substrate at a controlled speed.⁴ The PTFE blade (*ca.* 13 mm wide \times 0.5 mm thick) was first cleaned and conditioned by drawing several times across a clean silicon wafer at 270 °C, under a load of 750 g and at 0.6 mm s⁻¹. The silicon wafer was then discarded and replaced with either a fresh wafer or a gold coated glass microscope slide. The PTFE transfer film was deposited in a single sweep under identical conditions to those used for cleaning. Silicon wafer substrates (75 mm diameter, $\langle 100 \rangle$ orientation) were used as received from the supplier. The gold-coated slides were prepared by argon ion cleaning and vacuum deposition of *ca.* 1 nm of chromium to promote adhesion, followed by *ca.* 200 nm of gold.

Films of PFI were deposited onto *ca.* 12 \times 12 mm² pieces of the four different substrates (silicon, gold/glass, PTFE/silicon and PTFE/gold/glass) by heating a small quantity of the powder (Aldrich) in an electric crucible in vacuum (*ca.* 10⁻⁵ mbar). Under these conditions, PFI sublimates below its melting point (164 °C). The substrates were positioned *ca.* 30 mm above the crucible and held at room temperature. Films of PFI prepared in this way were sufficiently thick to give a metallic blue interference colour.

PFI/gold/glass and PFI/PTFE/gold/glass samples were studied by RAIRS using a Biorad FTS60 spectrometer with a wide-band MCT (mercury cadmium telluride) detector and a Spectratech FT80 specular reflectance accessory. The IR beam was incident at 80° to the normal of the sample plane and spectra were collected in the range 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹. Two hundred scans were coadded and ratioed against the spectrum of the relevant substrate as reference.

PFI/silicon and PFI/PTFE/silicon samples were analysed by XPS using a Scienta ESCA300 spectrometer. This employs a high-power rotating anode and monochromated Al-K α X-ray source ($h\nu = 1486.6$ eV), high transmission electron optics and a multichannel detector.^{28,29} The geometry of the X-ray

source, sample manipulator and electrostatic lens is such that at low electron take-off angle (θ , defined relative to the sample surface) the X-ray beam strikes the sample at grazing incidence. This gives enhanced sensitivity at low θ and is ideal for the study of thin films.²⁹ The samples were mounted on standard stubs with double-sided tape and analysed at ambient temperature. The pressure in the analysis chamber of the spectrometer was *ca.* 10^{-9} mbar, and the X-ray source power was 2.8 kW. Charge compensation was achieved using a low-energy electron flood gun (Scienta FG300) with settings adjusted to give minimum peak widths. Survey and C 1s, F 1s region spectra were recorded for each sample at $\theta=90^\circ$ and 10° . The entrance slit to the hemispherical analyser was 0.5 mm wide and a pass energy of 150 eV was used, giving an overall instrument resolution of *ca.* 0.32 eV.³⁰ Quantification was achieved using C 1s and F 1s sensitivity factors measured using clean PTFE tape. Total acquisition times for survey and region spectra at the two values of θ were *ca.* 40 min per sample. X-Ray-induced sample degradation during this time is judged to be insignificant. Some sublimation of the PFI films occurred during exposure to the vacuum system, detected by a lightening of the film interference colour after *ca.* 60 min in vacuum. However, the films were sufficiently thick that the sublimation did not affect the XPS data.

Results and Discussion

RAIRS

The IR spectrum of perfluoroicosane in the range 4000–400 cm^{-1} has been well documented^{6,31,32} and is known to consist of degenerate fundamental vibrations (E1 species), non-degenerate fundamentals (A2 species) and progression bands arising from interactions with the chain ends. The E1 species are polarised perpendicular to the molecular chain axis, the A2 species parallel, and the progression bands may be either perpendicular or parallel depending on the particular vibration. The E1 species occur at 1260–1150 and 560–550 cm^{-1} , whereas the A2 species occur at 650–630 and 535–520 cm^{-1} . The progression bands are spread across the entire spectrum.

RAIRS spectra of PFI/gold/glass and PFI/PTFE/gold/glass are shown in Fig. 1. The spectrum of PFI/gold/glass shows numerous vibrations, the strongest of which occur at 1373, 1340, 647, 545 and 531 cm^{-1} . The 1373, 1340 and 545 cm^{-1} vibrations are assigned to the parallel progression bands $\nu_2(2)$, $\nu_2(4)$ and $\nu_5(4)$, and the 647 and 531 cm^{-1} vibrations to the parallel fundamental bands A2(2) and A2(3), respectively. The E1 species appear as relatively weak bands at 1254, 1219 and 1150 cm^{-1} . They would normally dominate the transmission IR spectrum of a randomly oriented PFI sample, being

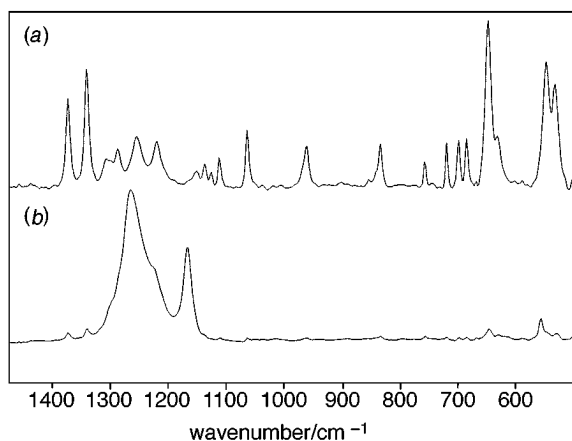


Fig. 1 RAIRS spectra of (a) PFI/gold/glass and (b) PFI/PTFE/gold/glass

considerably more intense than the A2 species. However, in RAIRS the metal surface selection rule allows only those vibrations with a transition dipole moment perpendicular to the surface to be observed.^{33,34} Hence, the occurrence of strong parallel polarised vibrations and weak perpendicular polarised vibrations implies that the PFI molecules are arranged with the molecular chain axis perpendicular to the substrate. The observation of weak E1 bands may be due to slight deviations of the molecular chains from perpendicular or to slight misalignment of the optical pathway of the spectrometer.

The RAIRS spectrum of PFI/PTFE/gold/glass is quite different from that of PFI/gold/glass. The strong parallel polarised vibrations have almost disappeared and new bands have appeared at 1296 (sh), 1283 (sh), 1264, 1230 (sh), 1166 and 556 cm^{-1} . The 1264, 1230, 1166 and 556 cm^{-1} vibrations are assigned to the perpendicular fundamental bands E1(1), E1(2), E1(3) and E1(4), and the 1296 and 1283 cm^{-1} vibrations to the perpendicular progression bands $\nu_2(7)$ and $\nu_2(8)$, respectively. The implication is that the molecular chain axis now lies parallel to the substrate surface. Again, the observation of weak parallel polarised bands may be due to slight deviations of the molecular chains from parallel to the substrate or to slight misalignment of the spectrometer.

The E1(1), E1(2) and E1(3) bands of PFI shift slightly on going from PFI/gold/glass to PFI/PTFE/gold/glass, *i.e.* from 1254, 1219 and 1150 cm^{-1} to 1264, 1230 and 1166 cm^{-1} , respectively. This may represent a small change in the structure of the molecule in going from 'naturally' grown material on a plain substrate to epitaxially grown material on a PTFE transfer film substrate.

XPS

XPS survey spectra of PFI/silicon and PFI/PTFE/silicon were identical, showing only C and F (see Fig. 2) Fig. 3 shows C 1s spectra of the samples at $\theta=90^\circ$ and 10° . The C 1s component at *ca.* 292.5 eV binding energy represents the CF_2 carbon atoms of the PFI chain and that at *ca.* 294.6 eV represents the CF_3 end groups.³⁵ At $\theta=90^\circ$ XPS samples to a depth of *ca.* 5 nm, whereas at $\theta=10^\circ$ it is more surface-sensitive, sampling to *ca.* 1 nm. The PFI molecular chain is *ca.* 2.5 nm long.²⁴ For PFI/silicon the $\text{CF}_3:\text{CF}_2$ intensity ratio increases on going from $\theta=90^\circ$ to 10° , consistent with PFI molecules oriented perpendicular to the substrate. This effect has been seen in other materials where the terminal CF_3 group of a perfluorinated alkyl chain is located at the uppermost surface of the sample.^{36,37} For PFI/PTFE/silicon the $\text{CF}_3:\text{CF}_2$ ratio remains unchanged as θ is reduced, consistent with PFI molecules aligned parallel to the substrate.

Table 1 shows quantification and curve-fit data for the samples. For PFI/PTFE/silicon the C:F atomic ratio is very close to the theoretical value for $\text{C}_{20}\text{F}_{42}$ at both $\theta=90^\circ$ and

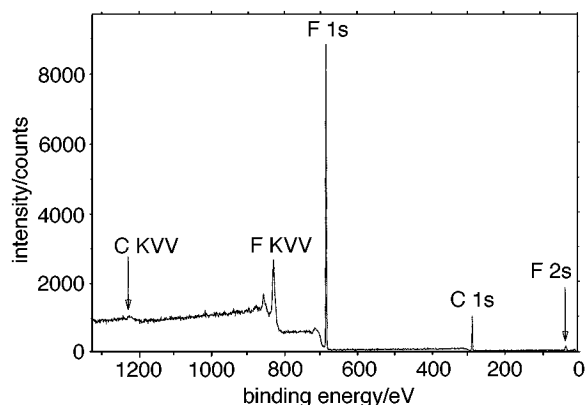


Fig. 2 XPS survey spectrum of PFI/silicon at $\theta=90^\circ$

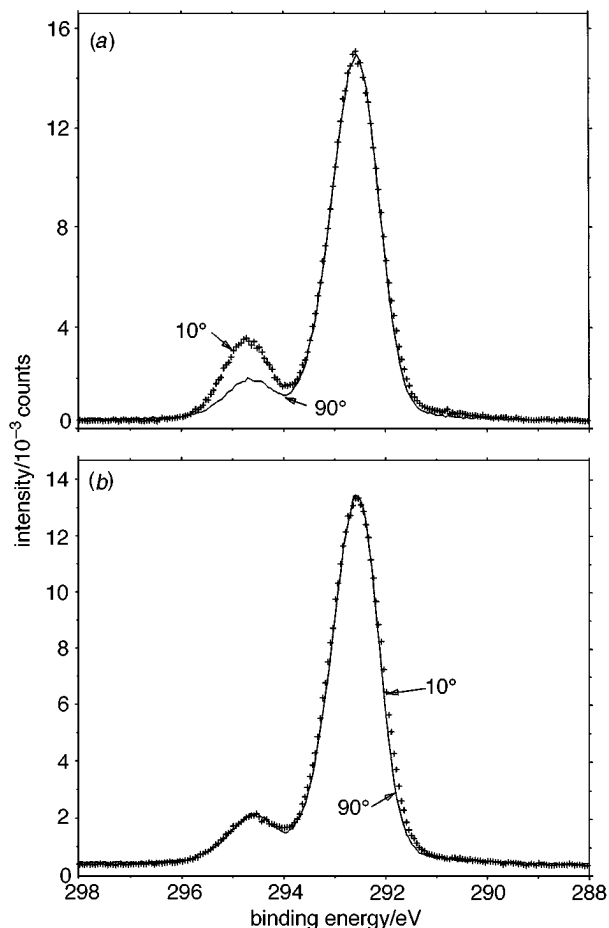


Fig. 3 XPS C 1s spectra at $\theta=90^\circ$ and 10° of (a) PFI/silicon and (b) PFI/PTFE/silicon

10° , consistent with PFI molecules aligned parallel to the substrate. For PFI/silicon the C:F atomic ratio decreases on going from $\theta=90^\circ$ to 10° , consistent with the perpendicular molecular orientation. However, it is surprising that at $\theta=90^\circ$ the C:F ratio shows an excess of carbon over the theoretical value. This may be due to a dependence of the C 1s and F 1s sensitivity factors (*via* the photoelectron inelastic mean free paths) on alignment between the electron take-off direction and the channels between the molecular chains.

Components representing CF_3 , CF_2 adjacent to CF_3 [$CF_2(2)$] and the remainder of the CF_2 units of the molecular chain [$CF_2(1)$] were fitted to the C 1s envelopes. The greater binding energy of $CF_2(2)$ relative to $CF_2(1)$ is a secondary chemical shift effect due to the additional β -position fluorine substituent.³⁸ A single component was fitted to the F 1s envelope. The C 1s curve fits were constrained to give equal areas for the CF_3 and $CF_2(2)$ components; a typical curve fit is shown in Fig. 4. After curve fitting the spectra were referenced to a binding energy of 292.48 eV for $CF_2(1)$, a recent literature

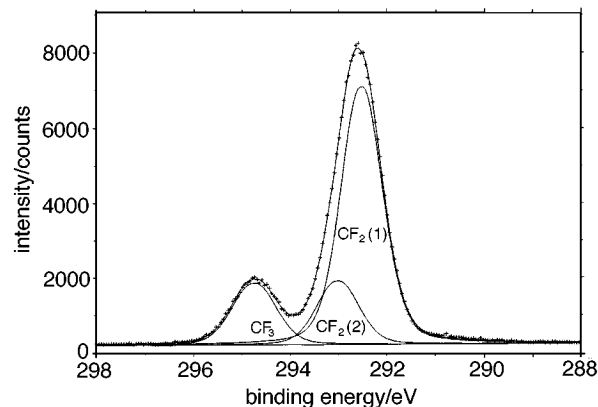


Fig. 4 C 1s curve-fit for PFI/silicon at $\theta=10^\circ$

value for PTFE.³⁸ The spectra shown in Fig. 3 and 4 are also binding energy referenced in this way.

For PFI/PTFE/silicon the C 1s curve-fit ratios for $CF_3:CF_2(2):CF_2(1)$ are very close to 10:10:80 at both $\theta=90^\circ$ and 10° , as expected for PFI molecules lying parallel to the substrate. For PFI/silicon the $CF_3:CF_2(2):CF_2(1)$ ratio changes from close to 10:10:80 at $\theta=90^\circ$ to 16.4:16.4:67.1 at $\theta=10^\circ$. Calculation of electron attenuation predicts that for PFI chains oriented perpendicular to the substrate the CF_3 :total CF_2 intensity ratio is given by:

$$CF_3/CF_2 = \frac{[1 + \exp(-19a)] \exp a}{1 - \exp(-18a)}$$

where $a = \Delta z / \lambda \sin \theta$, Δz is the displacement between successive CF_2 units along the chain axis and λ is the C 1s inelastic mean free path. With $\Delta z = 0.130 \text{ nm}^2$ and $\lambda = 3.0 \text{ nm}^3$ the CF_3/CF_2 intensity ratio is predicted to be 10.5:89.5 at $\theta=90^\circ$ and 22.4:77.6 at $\theta=10^\circ$. Hence the agreement at $\theta=90^\circ$ is good. The discrepancy at $\theta=10^\circ$ could be due to several factors, such as roughness and disorder of the sample surface on an atomic scale, the finite solid angle of collection of the spectrometer electron lens and small errors in setting θ .⁴⁰

Note that for PFI/silicon the C 1s CF_3 binding energy increases by *ca.* 0.10 eV, relative to $CF_2(1)$, on going from $\theta=90^\circ$ to 10° . The F 1s binding energy also increases by *ca.* 0.06 eV. This must be due to the different chemical environment of the surface CF_3 groups compared with the same groups deeper in the sample. Calculation shows that for PFI/silicon at $\theta=90^\circ$ the surface CF_3 group contributes <50% of the total C 1s CF_3 intensity, the remainder being due to CF_3 groups at the interface between the first and second molecular layers. However, at $\theta=10^\circ$ the C 1s CF_3 intensity is due entirely to the surface CF_3 group. Surface chemical shifts in polymer systems have been reported previously⁴¹ and are due to reduced intermolecular polarisation relaxation at the surface, resulting in slightly higher binding energies.⁴² The C 1s curve-fit binding energy for $CF_2(2)$ decreases by *ca.* 0.17 eV, relative to $CF_2(1)$, on going from $\theta=90^\circ$ to 10° . However, as $CF_2(2)$

Table 1 XPS quantification and curve-fit data at $\theta=90^\circ$ and 10° for PFI/silicon and PFI/PTFE/silicon

| sample | θ | C 1s curve-fit data | | | | | | | | | F 1s curve-fit E_B/eV |
|---------------------------|----------|---------------------|-----------|-----------------|-----------|--------|-----------|-----------|--------|--------|-----------------------------------|
| | | C (atom%) | F (atom%) | E_B/eV | | | atom% | | | | |
| | | | | $CF_2(1)$ | $CF_2(2)$ | CF_3 | $CF_2(1)$ | $CF_2(2)$ | CF_3 | | |
| theory ($C_{20}F_{42}$) | | 32.3 | 67.7 | | | | | 80 | 10 | 10 | |
| PFI/PTFE/Si | 90 | 32.4 | 67.6 | 292.48 | 293.13 | 294.56 | 79.1 | 10.4 | 10.4 | 689.69 | |
| | 10 | 32.7 | 67.3 | 292.48 | 293.11 | 294.58 | 79.7 | 10.2 | 10.2 | 689.70 | |
| PFI/Si | 90 | 35.5 | 64.5 | 292.48 | 293.14 | 294.60 | 80.8 | 9.6 | 9.6 | 689.71 | |
| | 10 | 32.8 | 67.2 | 292.48 | 292.97 | 294.70 | 67.1 | 16.4 | 16.4 | 689.77 | |

lies within the overall CF₂ envelope and as the constraint of equal CF₃ and CF₂(2) areas is less valid at $\theta = 10^\circ$ than at 90° , this observation is not as reliable as for the CF₃ group.

For PFI/PTFE/silicon no change is observed in the C 1s CF₃ or F 1s binding energies, relative to C 1s CF₂(1), as θ is reduced, and the values are very similar to those for PFI/silicon at $\theta = 90^\circ$. This is not surprising given the parallel orientation of the PFI molecules at the surface. In this arrangement the uppermost PFI molecules may show a surface chemical shift relative to those deeper in the sample, but 'internal' surface chemical shifts would not be expected.

Conclusion

Both XPS and RAIRS clearly demonstrate a difference in molecular orientation for PFI vapour deposited onto plain substrates (silicon and gold) and onto PTFE tribological transfer films. In PFI/silicon and PFI/gold/glass the PFI molecular chains orient perpendicular to the substrate, whereas in PFI/PTFE/silicon and PFI/PTFE/gold/glass they take up a parallel orientation. Because the structural parameters of bulk PFI and PTFE are very closely matched, this is probably a case of classical epitaxy. However, some authors⁹ have suggested that the structure of PTFE chains at the surface of a transfer film may be different from those in the bulk, in which case the graphoepitaxy effect of the aligned PTFE ribbons would be more important. We note a small frequency shift for the E1 vibrations of PFI on going from PFI/gold/glass to PFI/PTFE/gold/glass, which may represent a small difference in shape of the molecule in the two situations. For PFI/silicon, XPS reveals a surface chemical shift for the uppermost CF₃ groups of the sample.

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