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Etching of carbon fibres by argon ions

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The sputtering rate by argon ions was determined for five carbon fibres with different carbonization temperatures, and the rate was found to be in the range 3×10^{-3} to 8×10^{-3} μm/min, when an acceleration voltage of 2 kV was applied. The relation between the sputtering rate and the mechanical properties was examined. The sputtering rate and its yield increased with the decrease of the modulus of elasticity.

1. Introduction

Research and development of pitch-based carbon fibres is progressing rapidly. However, the manufacturing processes of pitch-based carbon fibres are still developing, because of the heterogeneity of the raw material. The correlations among the manufacturing conditions, the physical properties and the chemical structure of carbon fibres must be clarified as much as possible in order to attain this purpose. Many investigators have observed the surface of carbon fibres using Electron Spectroscopy for Chemical Analysis (ESCA) [1–4]. However, only a few studies have been done on physical structures of the skin layer [5–8].

In this study, the sputtering rate was determined for the skin layer of carbon fibres under given conditions. The relation between the sputtering rate and the physical properties are discussed for pitch-based carbon fibres.

2. Experimental procedure

2.1. Samples

Various carbon fibres are listed in Table I. Pitch-based carbon fibres having a diameter of 11.5–25 μm were used. The heat-treated temperature range was 1000–2500 °C.

2.2. ESCA

A Shimadzu X-ray photoelectron spectrometer ESCA-850 (Shimadzu Corporation, Kyoto, Japan) was used for etching the carbon fibres, using copper sheet as a reference. Argon ion etching was carried out under the following conditions: Ar, 4×10^{-4} Pa; acceleration voltage, 2 kV; ion beam current, 20 mA; and FOCUS, scale 6. Surface analysis was carried out at 8 kV with a current of 30 mA.

TABLE I Carbon fibres used in this study

Sample	Raw material	Carbonized temperature (°C)	Diameter (μm)
CF-1	pitch	1000	23.9
CF-2	pitch	1500	11.8
CF-3	pitch	2000	11.9
CF-4	pitch	2000	24.9
CF-5	pitch	2500	13.3

2.3. Scanning electron microscopy (SEM)

An Akashi scanning electron microscope ALPHA-30A (Akashi Seisakusho Ltd, Tokyo, Japan) was used for observing the marks of etching. The observations were carried out at the acceleration voltage of 15 kV, and emission current of 100 μA.

2.4. Ion coater

A IB-2 ion coater (Eiko Engineering Co., Ibaragi, Japan) was used for depositing gold on the surface of copper sheets. This coater was used only for determining the etching area with the naked eye.

2.5. Mechanical properties

JIS R 7601 "Testing method for single fibre" was applied for measuring the modulus of tensile elasticity of carbon fibres. The test specimen, i.e., a single fibre, was fixed by a suitable adhesive agent to the mount and tested using a TENSILON RTM-25 (ORIENTEC Co., Tokyo, Japan).

Stress–elongation curves were measured under the following conditions: the length of the test specimen is 25 mm, tensile speed 8.0 mm/min, and full scale 0.1 kg. The mechanical properties adopted were the average of 50 measurements.

The tensile strength is given by P/A, where P (N) is the stress at break, and A (mm^2) the cross-section of the fibre. The modulus of tensile elasticity, E, is given by

$$E = \left(\frac{P}{A} \times \frac{L}{\Delta L}\right) \Big/ \left(1 - \frac{P}{\Delta L} \times K\right) \quad (1)$$

where K (mm/N) is the correction parameter of the equipment for compliance. The elongation ΔL(mm) is obtained from the value $L - L_0$, where L_0 is the

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length of a carbon fibre at zero stress, and L is the length at break.

2.6. The etching area

In the measurement of the sputtering rate of this study, samples were etched without scanning by an argon ion beam until we could clearly confirm the boundary between the etched part and the masked part. In general, the sputtering rate varies depending upon the size of the irradiated area. To evaluate the sputtering rate theoretically, the size of the irradiated area must be measured accurately in advance. So the number "FOCUS" for focusing the ion beam was varied, where FOCUS is the special name of the knob controlling the beam size in the instrument, and the etched area for each FOCUS number was measured.

At first, the copper foil (type CF-T8, thickness 3 μm, Fukuda Kinzoku Co., Osaka, Japan) was cut so as to fit the size of the sample stand (φ10), and gold was evaporated on to it to a thickness of 30 nm with the ion coater. This sample was pasted (SILVEST P-255, Tokuriki Chemical Lab, Tokyo, Japan) on to the sample stand with the silver paste. The sample was etched in various numbers of FOCUS for 10 min. Pictures were taken for each etched sample, and the size of the etching area was measured, as shown in Fig. 1. The relation between the size of the etching area and FOCUS is shown in Fig. 2. The ion beam was focused most appropriately on the sample when FOCUS was set to 6, and the size of the etching area was 24.6 mm^2. The shape of the etching area was an ellipse, rather than a circle in this study. This was caused by the fact that the ion beam was irradiated at an angle 30° of the horizontal plane.

The surface of the copper sheet was coated with gold to a thickness of 30 nm to facilitate the detection of the boundary between the etching part and the masked one with the naked eye. A half of this sample was masked by commercial aluminium foil, as shown in Fig. 3. More than ten filaments of a carbon fibre were stuck to the edge of the copper sheet by double sided tape so that the sputtered depth was easily detected by SEM. The copper sheet was used as a substrate for the carbon fibres so as to be easily transferred to the sample stand of the scanning electron microscope. After etching by ESCA, the carbon fibres were observed by SEM and the etching depth was read from the photograph. This was followed by a calculation of the sputtering rate.

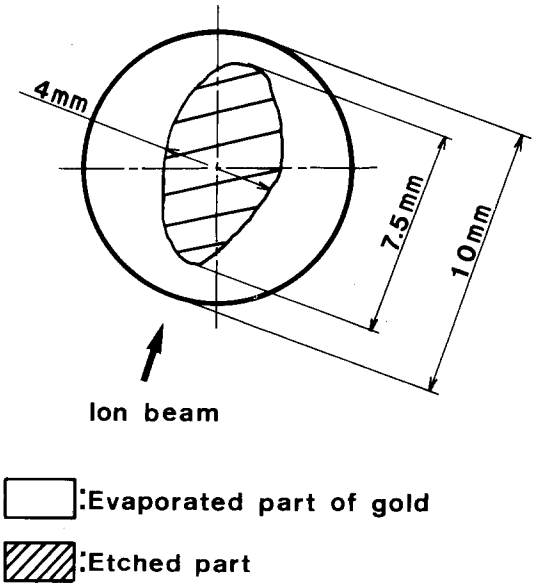

Figure 1 Shape of etched part at FOCUS 6.

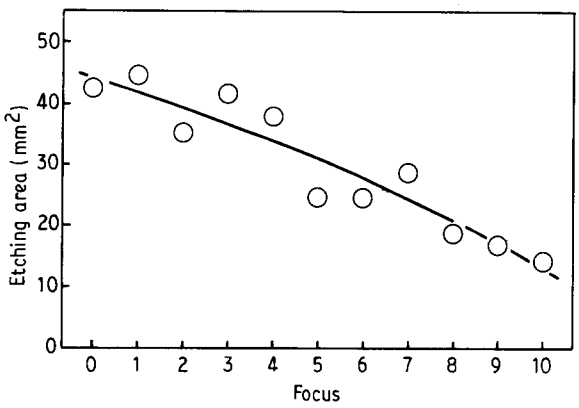

Figure 2 Relation between etching area and FOCUS.

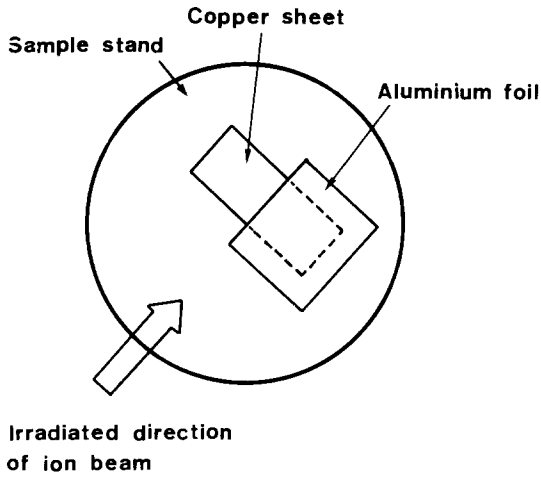

Figure 3 Sample stand and sample (copper).

3. Results and discussion

3.1. Mechanical properties of the carbon fibres

The mechanical properties of the carbon fibres are shown in Table II. The modulus of elasticity is in the range 70–280 GPa, and tensile strength in the range 0.6–1.6 GPa.

3.2. Sputtering of the copper sheet

The copper sheet was initially etched in order to confirm the adequacy of our experimental conditions. Fig. 4 shows the surface of the copper sheet etched for 1000 min. The left side indicates the etched part, and the right side the part masked by aluminium foil. The etching depth can be easily measured. The slightly rough surface of the etched part may arise from the

TABLE II Mechanical properties of carbon fibres

Sample	Modulus of elasticity (GPa)	Tensile strength (GPa)	Elongation (%)
CF-1	109	0.81	0.73
CF-2	78	0.66	0.84
CF-3	150	0.61	0.43
CF-4	162	1.55	0.99
CF-5	271	1.54	0.60

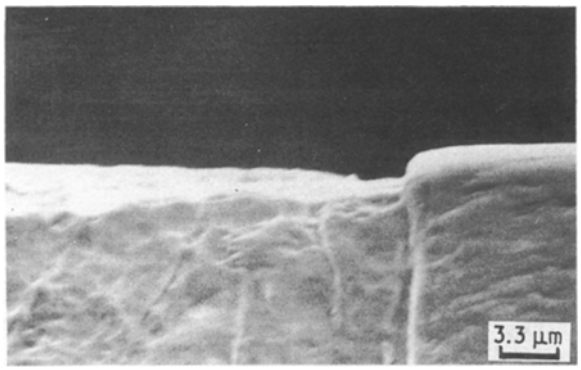

Figure 4 Copper (after etching).

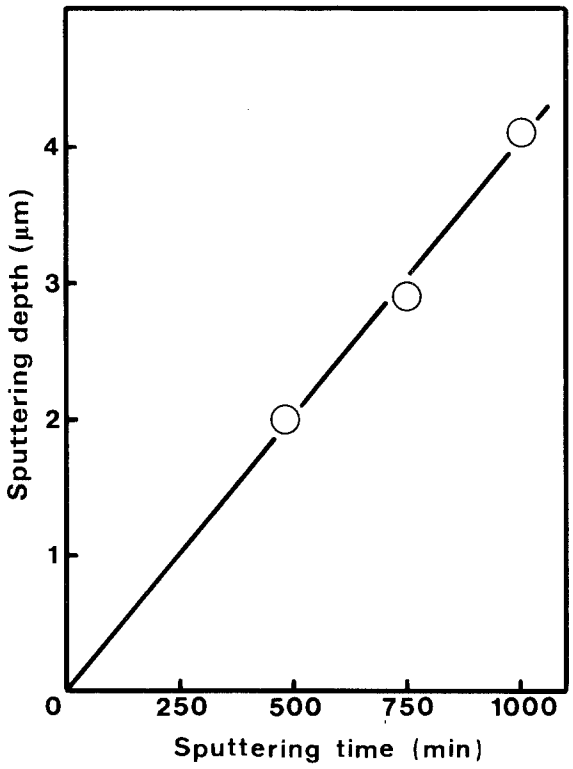

Figure 5 Sputtering rate of copper.

fact that the ion beam and the properties of the copper sheet are not completely uniform. The linear relationship between the sputtering time and the depth was confirmed as shown in Fig. 5. Thus, the sputtering rate Z_e of 4.1 nm min^{-1} was experimentally obtained.

The theoretical expression for the sputtering rate Z_t is given by [9]

$$Z_t = \frac{M}{\rho \times N \times e} \times S_M \times j_p \qquad (2)$$

The theoretical sputtering rate was obtained for copper sheet by putting the following values into Equation 2: the atomic mass M = 63.55 g mol^{-1}; the density $\rho = 8.92$ g cm^{-1}; Avogadro's number $N = 6.023 \times 10^{23}$ mol^{-1}; the elementary charge $e = 1.602 \times 10^{-19}$ C, the sputtering yield $S_M = 4.3$ (Argon ion energy, 2 kV) [10], and the primary ion current density $j_p = 5.5 \times 10^{-6}$ A.

The rate Z_t is 1.75×10^{-9} cm^3 sec^{-1}. This value is expressed by the etching volume per unit time. The value was divided by the size of the irradiated area (24.6 mm^2) of the ion beam (voltage: 2kV, FOCUS: 6), and the sputtering rate was given as $Z_t = 4.266$ nm min^{-1}. Z_e is nearly equal to Z_t, and this fact proves that our experimental conditions are appropriate for the determination of the sputtering rate for carbon fibres.

3.3. Sputtering of carbon fibres

A carbon fibre was etched for 500 minutes, and the photograph is shown in Fig. 6. The boundary between the etched part and the masked part can be clearly distinguished. However, it is not easy to determine the etching depth because the cross-section of the carbon fibre is a circle, unlike the copper sheet. The sputtering depth was determined as follows. We assumed that the carbon fibre was etched as in Fig. 7. Five points were chosen in the etched part, and the depths Z_2, and Z_1

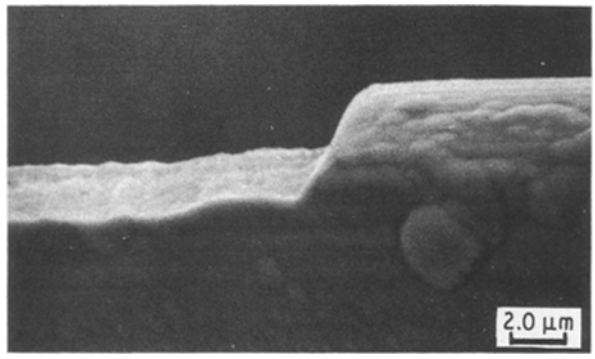

Figure 6 Carbon fibre (after etching).

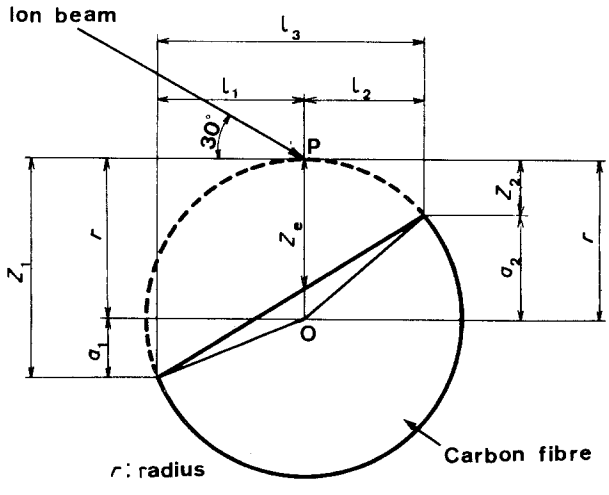

Figure 7 Sectional diagram of carbon fibre (after etching).

were read from the photograph. We need to calculate the sputtering depth Z_e at the position P, when the ion beam is irradiated at an angle of 30° to the horizontal plane. Then

$$a_1 = Z_1 - r \quad (3)$$

$$a_2 = r - Z_2 \quad (4)$$

where r is the radius of a carbon fibre.

$$l_1 = (r^2 - a_1^2)^{1/2} \quad (5)$$

$$l_2 = (r^2 - a_2^2)^{1/2} \quad (6)$$

$$l_3 = l_1 + l_2 \quad (7)$$

If we regard the relation between l_2 and Z_e as linear function, Z_e can be described as,

$$Z_e = \frac{Z_1 - Z_2}{l_3} \times l_2 + Z_2 \quad (8)$$

By using Equations 3–8, we obtain

$$Z_e = \frac{Z_1 - Z_2}{[Z_1(2r - Z_1)]^{1/2} + [Z_2(2r - Z_2)]^{1/2}} \times l_2 + Z_2 \quad (9)$$

For example, in the case of CF-5, the depth Z_e is 1.77 μm, and the sputtering rate is 3.42×10^{-3} μm min^{-1}.

3.4. Relation between the sputtering rate and the modulus of elasticity

Five carbon fibres were etched for 500 min, and the sputtering rates were obtained. The sputtering rate was plotted against the modulus of elasticity, and the result is shown in Fig. 8. The modulus of elasticity is inversely proportional to the sputtering rate: the carbon fibre having a small modulus of elasticity (soft carbon fibre) has a large sputtering rate, so is easier to etch than a fibre having large modulus of elasticity. A linear relation is derived as follows,

$$Z_e = -0.19E + 8.59 \quad (10)$$

where E is the modulus of elasticity.

The photographs of the cross-section for CF-2 and CF-5 are shown in Fig. 9a and b. From these photographs, it is clear that CF-2 is radial and coarse. On the other hand, CF-5 has an onion skin radial structure [11, 12] and is more dense than CF-2. We can conclude that the more the inner part of a carbon fibre becomes dense, the more the modulus of elasticity increases. This tendency is coincident with that in orientation of crystal lattice [13–15]. The relation between the tensile strength and the sputtering rate is shown in Fig. 10. This relation is not as clear as the above one. However, we can say that the larger the tensile strength, the smaller the sputtering rate. These sputtering results may come from the fact that the tensile strength depends not only on the interatomic force, but also on the defects in the structure.

3.5. The sputtering yield

The sputtering yield S_M was calculated by Equation 2 from the experimental values of Z_e. The relation between the sputtering yield and the modulus of elasticity is shown in Fig. 11. From this relation, a carbon fibre having a small modulus of elasticity shows large sputtering yield, and the more the modulus of elasticity increases, the less the sputtering yield decreases.

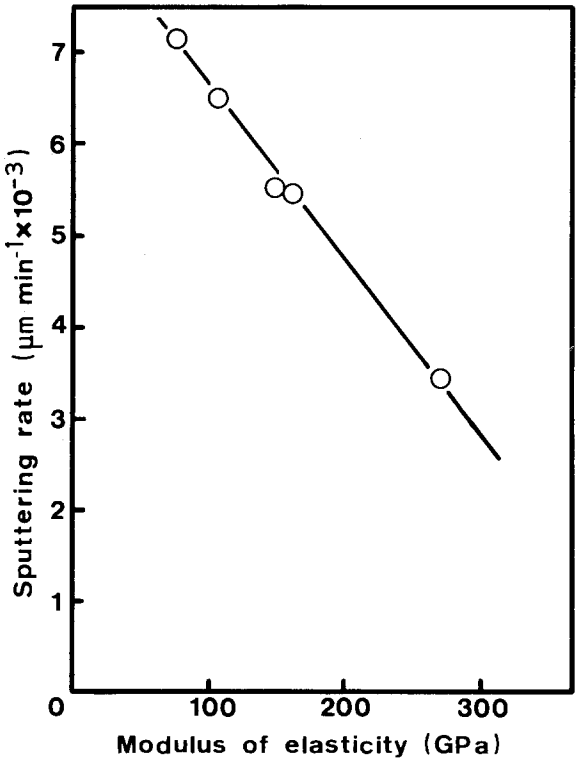

Figure 8 Relation between modulus of elasticity and sputtering rate.

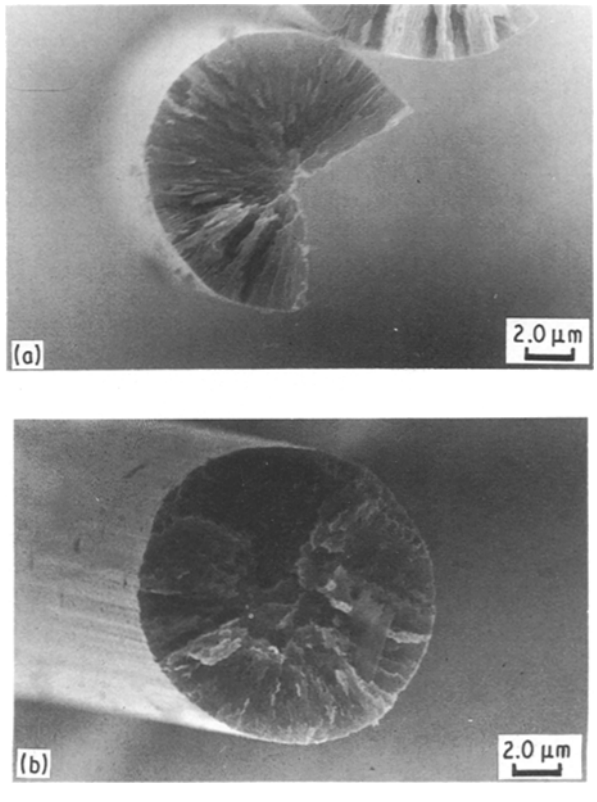

Figure 9 Sectional diagram of carbon fibres: (a) CF-2; (b) CF-5.

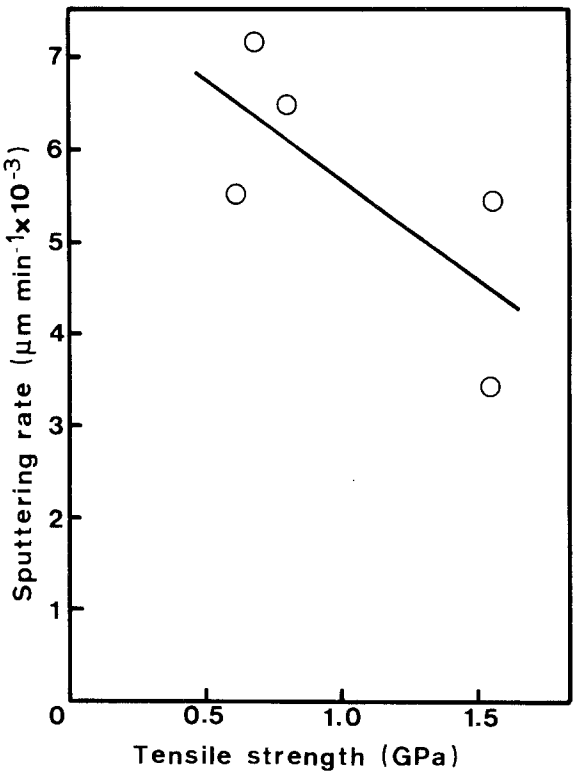

Figure 10 Relation between tensile strength and sputtering rate.

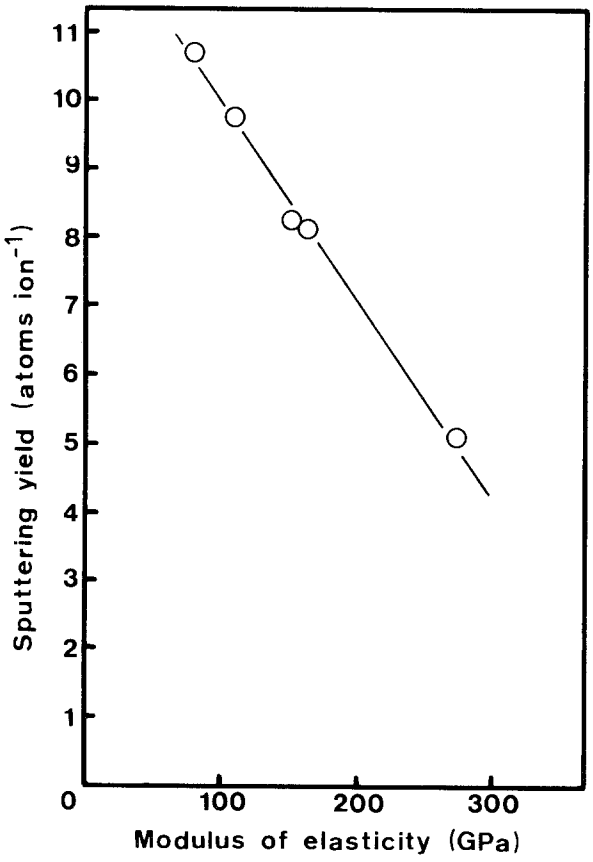

Figure 11 Relation between sputtering yield and modulus of elasticity.

The relation is expressed as follows

$$S_M = -0.28E + 12.82 \quad (11)$$

This fact reveals that the sputtering yield will vary greatly even among carbon fibres produced in the same manner. We find that $S_M = 6.02$ from Equation 9 for T-300 (Toray Industries Inc., Tokyo, Japan) which is a PAN-based carbon fibre. However, this value is larger than the value 0.5 (Ar^+ ion, 2kV) which was roughly estimated from the literature [16]. This discrepancy will come from the substantial difference in the properties of the carbon fibres, although concrete experimental conditions are not clear for this reference value. Therefore, the applicability of Equation 9 is doubtful for PAN-based carbon fibres.

3.6. Structure of the sputtered surface

Depth profiles of photoelectron spectra on CF-2 are shown in Figs 12 and 13, and that on CF-5 are shown in Figs 14 and 15. CF-2 has the lowest modulus of elasticity and CF-5 the highest among the samples tested. The sputtering depth for each spectrum was calculated from the sputtering rate of each carbon fibre and is shown on the right of the figure. From Figs 12 and 14, the peak position of the C_{1s} spectra changes only slightly with the increase of depth. This result suggests that the components of these carbon fibres are almost homogeneous. From Figs 13 and 15, the oxygen content in CF-2 seems to be higher than that in CF-5. In fact, the oxygen content of the surface layer is higher than that of other layers in the entire region etched, as shown in Table III. This comes from the fact that the carbonized temperature of CF-2 is lower than that of CF-5. At any rate, the influence of selective sputtering at etching can be ignored in this case [17–19].

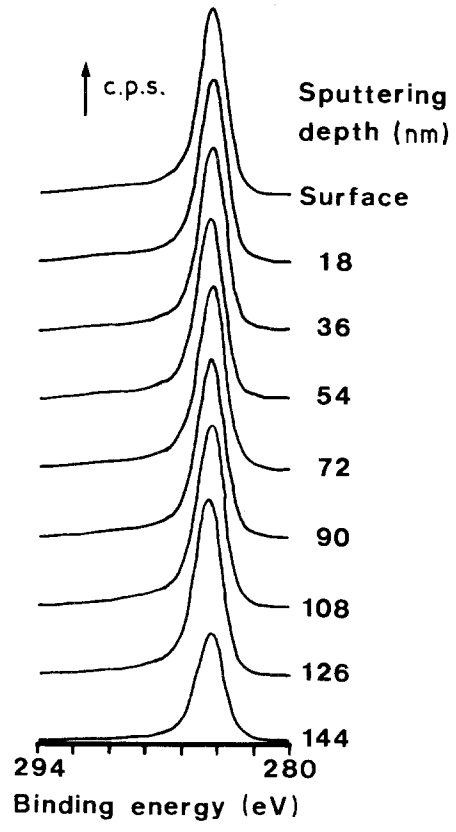

Figure 12 Depth profile of CF-2 (C_{1s} spectra).

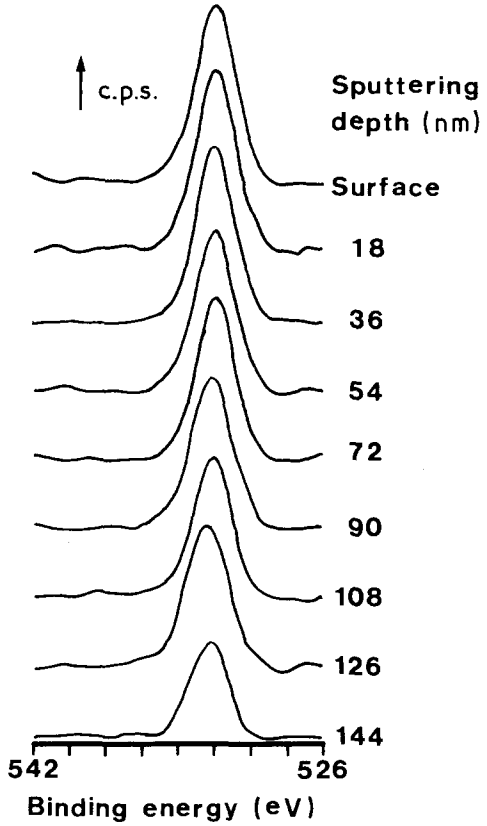

Figure 13 Depth profile of CF-2 (O_{1s} spectra).

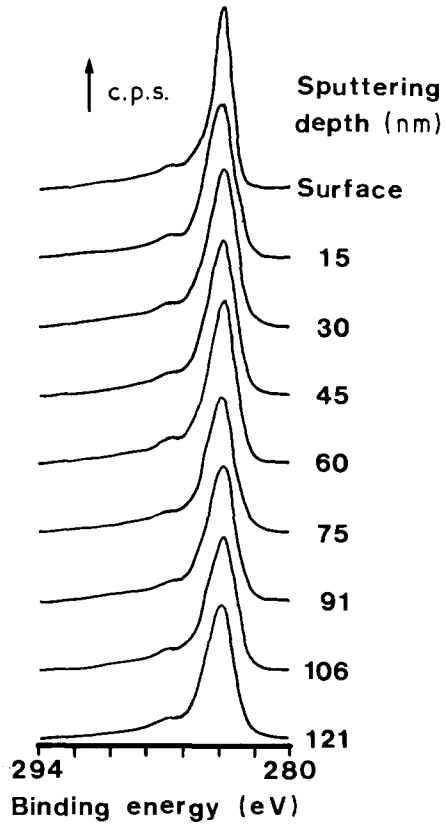

Figure 14 Depth profile of CF-5 (C_{1s} spectra).

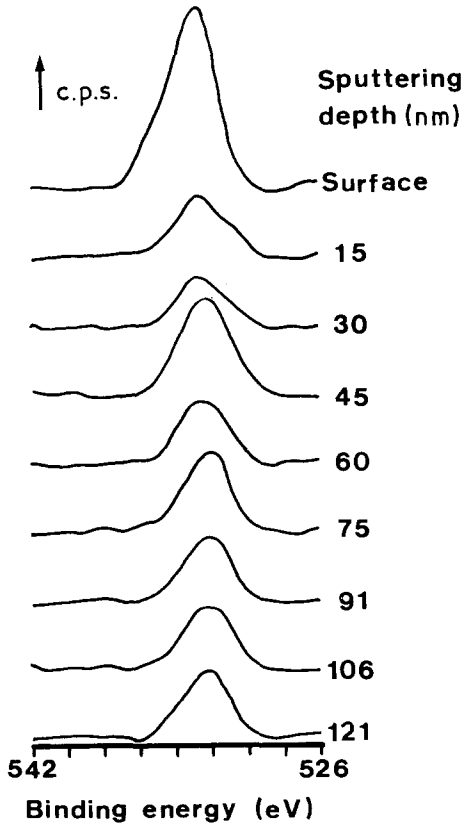

Figure 15 Depth profile of CF-5 (O_{1s} spectra).

TABLE III O_{1s}/C_{1s} ratios as a function of depth

CF-2									
Sputtering depth (nm)	0	18	36	54	72	90	108	126	144
O_{1s}/C_{1s} (%)	8.84	8.90	8.01	7.58	7.41	7.69	6.81	7.54	6.98
CF-5									
Sputtering depth (nm)	0	15	30	45	60	75	91	106	121
O_{1s}/C_{1s} (%)	10.28	3.82	2.70	5.46	3.35	5.03	3.93	4.34	3.90

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