

XPS를 이용한 흑연섬유의 표면분석

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Graphite Fiber Surface Analysis Using X-ray Photoelectron Spectroscopy

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요 약 : XPS를 이용하여 상업적으로 생산되는 흑연섬유의 표면산화상태에 관한 화학정보를 조사하였다. 이들 섬유들의 표면 관능기를 변화시키기 위하여 진공하에서 가열하거나 전기화학적으로 처리하였다. 피이크 디콘볼루션에 의하면 섬유표면은 히드록시기 또는 에테르기, 카르보닐기 및 카르복실산기로 구성되어 있으며 이들의 구성비는 표면처리에 따라 현저한 차이를 보였다. 아르곤 이온 에칭 실험결과 섬유와 매트릭스간의 계면접착력을 증가시키기 위하여 상업적으로 처리된 섬유에는 대부분의 산소관능기가 표면에만 존재하는 표면이질성이 밝혀졌다.

Abstract : X-ray photoelectron spectroscopy(XPS) was used to obtain the detailed chemical bonding information on surface oxides of the surface-modified graphite fibers. The commercial fibers were further heat-treated under vacuum or electrochemically treated to modify the surface. Deconvolution results of XPS spectra showed that the surface of the fibers was mostly composed of hydroxyl or ether, carbonyl and carboxylic acid groups but their compositions were varied upon surface treatments. An ionized argon etching experiment revealed surface heterogeneity that most oxygen was present only on the surfaces of commercially treated fibers, which results in improved adhesion between the fibers and matrices.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is a well known surface analysis technique and has been extensively used for studying the surface of fibers and polymers.^{1,2} Of XPS information, the most valuable is the chemical bonding information by measurement of the chemical shift; photoejected electrons are very sensitive to chemical environment. A special advantage of using XPS in a graphite fiber surface study is that the results are not disturbed by an intense photon absorption of carbon, which makes other spectroscopic techniques unsuitable. Another advantage is the ability of XPS to measure surface concentrations. This surface sensitivity comes from the fact that the escape depths of electrons are between 10 and 20 Å.

Since Barber et al.³ first used XPS to investigate the atomic composition of carbon fiber surfaces, the potential usefulness of XPS in carbon fiber studies has been shown by other researchers.^{4~9} The present work is concerned with elemental analysis of fiber surfaces and quantitative analysis of oxygen functional groups present on the fiber surfaces.

EXPERIMENTAL

Materials and Surface Treatments

Two types of PAN-based carbon fibers were examined as received: commercially available Hercules AU4, AS4 and Great Lakes Fortafil 3T. Fiber bundles from Hercules and Great Lakes Corp. consist of 10,000 and 30,000 single filaments, respectively. AS4 fibers had been commercially treated from AU4 fibers for better adhesion between the fibers and matrices. AS4 fibers were further treated electrochemically in a glass H-cell containing 0.05 N aqueous sulfuric acid solution. The 5 cm long carbon fibers were positioned in the larger compartment and a platinum electrode, used as a counter electrode, was in the small compartment. The distance between the electrodes was fixed at 5.0 cm. The electrochemical reduction

or oxidation was done by supplying a constant potential of ± 1.0 V between two electrodes for 15 min. In order to remove physically adsorbed oxygen, AS4 fibers were dried in a vacuum oven at 300 °C for 3 hours or heated in the XPS chamber at 300 °C for 30 min. The sample heating in the XPS was done by passing an electrical current through the holding rod and thus the sample was never exposed to the laboratory atmosphere. The sample dried in the oven, however, was exposed to air prior to analysis.

XPS Apparatus

The XPS spectra were obtained by AlK α radiation at 1486.6 eV. The instrument used was a Leybold Heraeus spectrometer (LHS 10) with a hemispherical analyzer. The binding energy of the gold 4f_{7/2} line was taken as 83.8 eV and was used for calibration of the instrument. The binding energies have not been corrected for the work function of the spectrometer and for charging effects caused by ionizing radiation, since the graphite fibers are good conductors.

The samples examined were prepared by placing cut fibers parallel on a copper holder. The fibers were held in place by a copper mask on top of the fibers and the sample was then secured on top of the sample holding rod. All measurements were performed at a pressure of 5×10^{-9} mbar, while sample transfers were made in the air. Each spectrum was scanned until a sufficiently large number of counts had been accumulated. The analyzer was operated in a retarding mode with pass energies (PE) of 200, 150, 50 or 20 eV. The different pass energies were used to compromise the sensitivity and resolution of spectra, depending on the measurement purposes. Wide scans were done to identify the elements present at high sensitivity (PE=200) and then narrow scans were done for quantitative elemental analysis at better resolution (PE=150). Finally, for detecting small spectral changes, a PE of 50 or 20 eV was used with a long time.

The depth profiling of fiber surfaces was performed by Ar⁺ etching under the following condi-

tions: pressure of Ar gas, 1×10^{-6} mbar; potential of Ar^+ , 5000 eV; beam current, 10 mA.

RESULTS AND DISCUSSION

Elemental Analysis

The wide scans on the fiber surfaces are shown in Fig. 1. They show that carbon fibers mainly consist of carbon and oxygen and that small amounts of nitrogen, sodium, chlorine and sulfur are also present.

Fig. 2 and 3 show the typical detailed scans of carbon and oxygen peaks. The carbon peak (C_{1s}) is broad and asymmetric with a long tail at the higher binding energy side, suggesting that more than one type of carbon exists on the fiber surface (ordinary chemical shift). However, the tail cannot be explained by chemical shift alone because it extends at least 5 eV beyond the end of the normal peak; this asymmetry has also been found in graphite single crystals.³ Therefore, it may be explained by inelastic photo-emission together with an ordinary chemical shift. The oxygen peak (O_{1s}) is also broad and asymmetric, which also indicates the presence of more than one type of oxygen in the surface layer. In general, the carbon peak is more informative than the oxygen peak because O_{1s} shifts are not so large and full width at half maximum (FWHM) of O_{1s} is larger than that of the corresponding C_{1s} signal.¹ The greater the half width, the greater the difficulty in peak resolution. The FWHMs of C_{1s} and O_{1s} measured from Fig.

2 and 3 were 1.9 and 3.5 eV, respectively.

The elemental compositions were determined by the relationship

$$C_x = \frac{A_x}{N_x R_x}$$

where C is the concentration, A is the peak area, N is the scan numbers, R is the sensitivity factor and the subscript x refers to the element of interest. The results are summarized in Table 1. It shows that the carbon content of all the samples is much lower than the overall carbon content of 95% due to a high concentration of oxygen present on the surface layer. AS4 fibers have much higher content of oxygen as compared to AU4 fibers; the oxygen content on the AS4 fibers was observed to be a factor of 3 higher than that on the AU4 fibers. It is believed that this increased oxygen content results in better adhesion at the interface of carbon fiber composites. Although the source of nitrogen is not precisely known, the relatively high con-

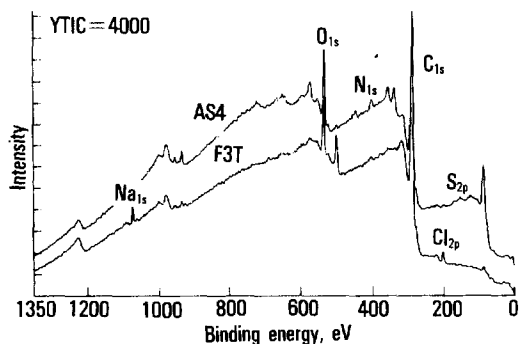


Fig. 1. XPS wide scan of graphite fiber surfaces.

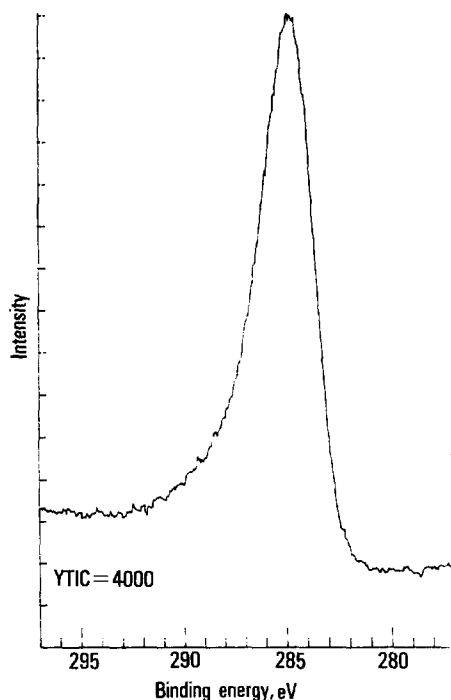


Fig. 2. XPS detailed spectrum of carbon (C_{1s}).

Table 1. Elemental Composition of Fiber Surfaces

Sample	C _{1s}	O _{1s}	N _{1s}	Na _{1s}	Cl _{2p}	S _{2p}	O/C
AS4	81.3	15.1	2.6	0.3	0.3	0.4	0.19
AS4/D	81.3	15.1	2.5	0.3	0.3	0.5	0.19
AS4/H	N. A	N. A	N. A	N. A	N. A	N. A	0.13
AS4/ER	84.6	12.0	2.7	0.2	0.2	0.3	0.14
AS4/EO	75.1	22.0	2.4	0.2	0.0	0.3	0.29
F3T	83.3	10.3	1.1	3.1	1.8	0.4	0.12
AU4	N. A	N. A	N. A	N. A	N. A	N. A	0.05

AS4 : AS4 fibers, as received

AS4/D : AS4 fibers, dried in a vacuum oven

AS4/H : AS4 fibers, heated in the XPS instrument

AS4/EO : AS4 fibers, electrochemically oxidized

AS4/ER : AS4 fibers, electrochemically reduced

F3T : Fortafil 3T

AU4 : Hercules fibers, surface untreated¹³

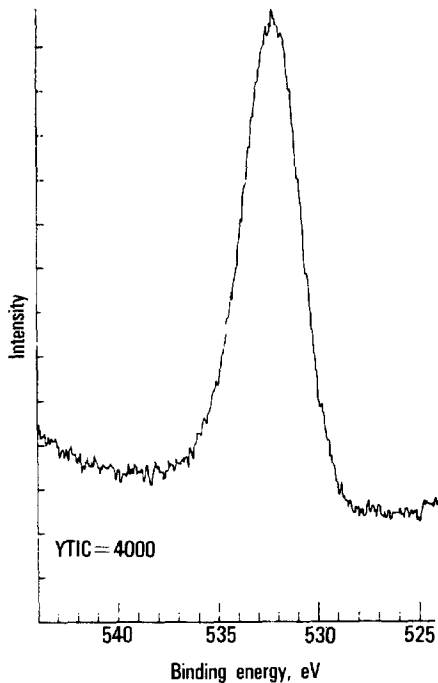


Fig. 3. XPS detailed spectrum of oxygen (O_{1s}).

tent of nitrogen in AS4 fibers may indicate that they were oxidized in nitric acid solution. Hammer et al.⁴ attributed the presence of nitrogen to residual material from ineffective graphitization or

from the spinning operation (NaSCN). As compared to AS4, Fortafil 3T (sample F3T) fibers have a higher concentration of sodium, which will reduce their thermal oxidative stability.¹⁰ The sodium may come from residual sodium thiocyanate left over from the polymerization of acrylonitrile. Sulfur has been found in all PAN-based fibers.^{11,12} Chlorine could have been formed as a result of the oxidation of fibers (hypochlorite). An Auger study indicated that all trace amounts of the elements are situated between the graphite basal planes.⁶

The fibers AS4/D, which were dried in a vacuum oven to remove physically adsorbed oxygen, show virtually no changes in the elemental compositions compared to undried fibers (AS4). Since the fibers were already highly oxidized, the vacuum-drying apparently did cause neither further oxidation nor oxygen removal. Hammer et al.⁵ also found no change in oxygen content on vacuum-dried AS4 fibers at 300 °C for 12 hours, while the same treatment on AU4 fibers increased the oxygen content by 30%, suggesting that a large portion of the fiber surface was oxidized either during vacuum treatment or as the fibers were exposed to air and atmospheric moisture. On the other hand, a sample heated inside the XPS instrument (AS4/H) shows a 32% loss in O/C ratio as compa-

red to the sample AS4. Fig. 4 and 5 show negligible changes in peak shapes of carbon and oxygen between AS4 and AS4/H, which may indicate that little physisorbed oxygen is present on the fiber surfaces. These figures also show small peak shifts of C_{1s} and O_{1s} toward lower binding energy, which may be related to the conversion of carbon-oxygen bonding during heating. Therefore, the loss of oxygen concentration may be due to conversion of C-O bonding to C-C bonds, which will be discussed in the following section. Hopfgarten¹⁴ observed a small change in oxygen content upon heating at 200 °C inside the spectrometer.

Electrochemical treatments give results as expected: a large increase in oxygen content upon oxidation (AS4/EO) and a decrease upon reduction (AS4/ER).

Deconvolution of Carbon and Oxygen Peaks

Scola¹⁵ found that there were at least four oxygen functional groups on the carbon fiber surfaces: alcohol, carbonyl, lactone and carboxylic

acid. Clark et al.^{16~22} suggested an additive rule of C_{1s} chemical shifts, predicting a higher binding energy of 1.5 eV per single C-O bond in a polymer system. Proctor^{7,23} calculated the chemical shifts in carbon fiber spectra using the relaxation potential model. His result does not agree with the additive rule, which may reflect that chemical shifts in carbon fibers may be more complex than in polymers.

In this section, deconvolution results of our C_{1s} and O_{1s} spectra will be discussed as a means of more quantitatively characterizing oxygen functional groups present on the fibers. Smoothing of spectra was not done, to avoid erroneous data which may be introduced during such manipulation. Inelastic background scattering was corrected by an S-curve to increase the uniformity of curve fittings. In a series of fits to AS4 and F3T (control) fibers, the following results were obtained:

1. A Gaussian-Lorentzian mixing ratio of 0.65 gave the best fit. A mixing ratio of 1.0 means a

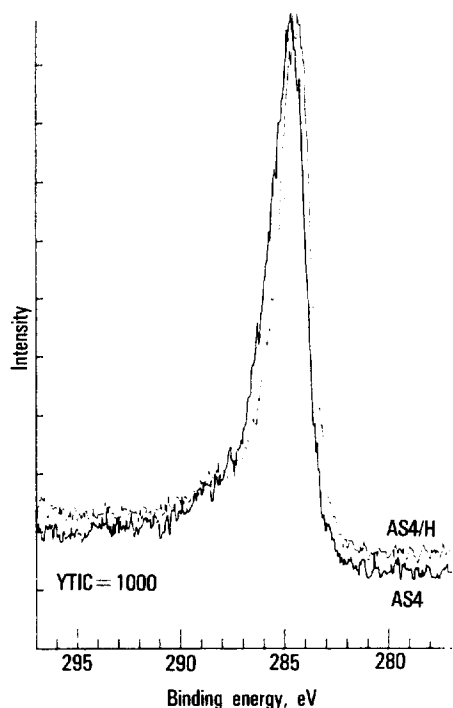


Fig. 4. Comparison of carbon spectrum of sample AS4 with that of AS4/H.

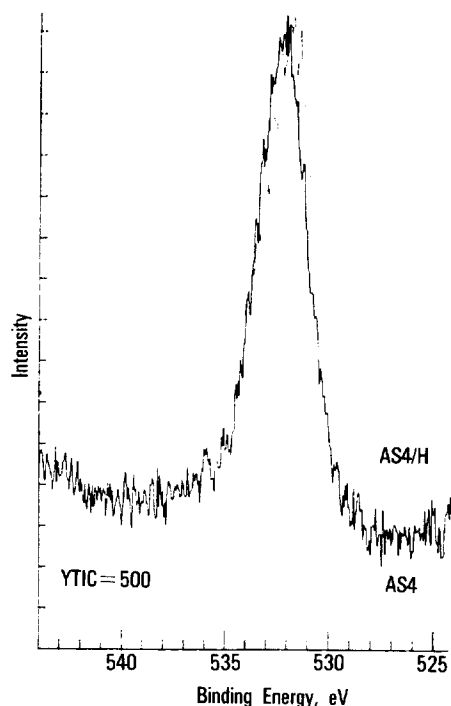


Fig. 5. Comparison of oxygen spectrum of sample AS4 with that of AS4/H.

pure Gaussian peak.

2. At least two oxide peaks in C_{1s} should be included to fit the carbon peak. These oxide peaks covered a wide range of binding energies; therefore, four oxide peaks were chosen in the fittings.

3. In the case of oxygen peaks, three peaks were selected for the best fit. The curve fittings were done using the parameters determined from control fibers. The position and width of oxide peaks were fixed, and the intensity and the S-curve were varied to obtain the best results (Table 2).

Fig. 6~10 show the results of curve fittings to C_{1s} spectra and the deconvoluted peak areas are tabulated in Table 3 as a percentage. Since there is doubt about the validity of the fifth peak, which was introduced for better fitting, the discussion will be confined to the other three oxide peaks.

From the area ratios in Table 3, surface oxides of AS4 fibers consist of 67% hydroxyl or ether type oxygen, 20% carbonyl type oxygen, and 11%

Table 2. Curve Fitting Parameters for Carbon Spectra

(unit : eV)					
Fiber	C-C	C-O	C=O	O=C-OH	Others
AS4	284.60	285.90	287.63	288.94	291.51
	(1.59)	(1.62)	(2.10)	(2.13)	(2.50)
F3T	284.50	285.90	287.63	288.94	290.72
	(1.72)	(1.75)	(2.10)	(2.13)	(2.50)

(number) : FWHM

Table 3. Results of Curve Deconvolution of C_{1s} Spectra

Sample	Peak Area, %				
	C-C (0.00)	C-O (1.30)	C=O (3.03)	O=C-OH (4.34)	Others (6.50)
AS4	65.98	22.79	6.73	3.60	0.90
AS4/H	74.76	12.45	7.35	5.44	0.00
AS4/EO	60.20	23.87	8.48	7.45	0.00
AS4/ER	77.68	14.70	5.54	2.08	0.00
F3T	71.15	21.46	3.13	2.47	1.79

(number) : chemical shift, eV

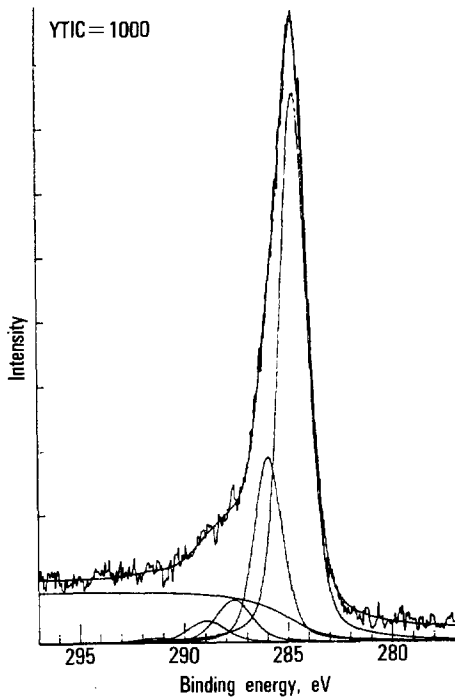


Fig. 6. Deconvolution of carbon spectrum of sample AS4.

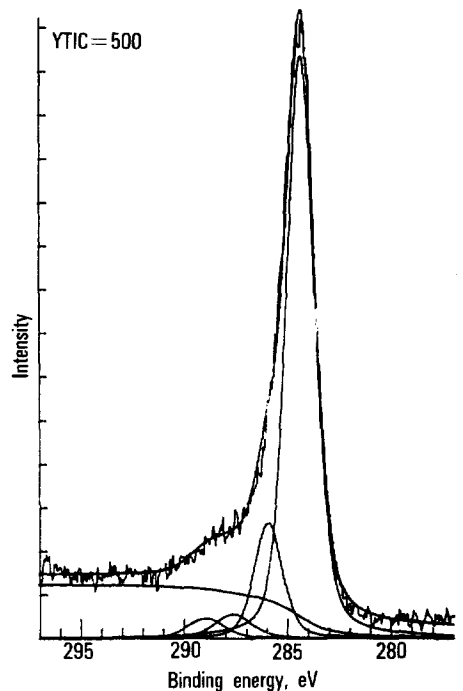


Fig. 7. Deconvolution of carbon spectrum of sample AS4/H.

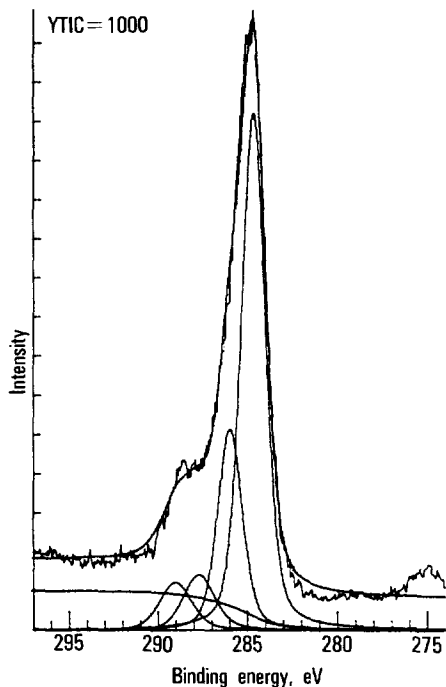


Fig. 8. Deconvolution of carbon spectrum of sample AS4/EO.

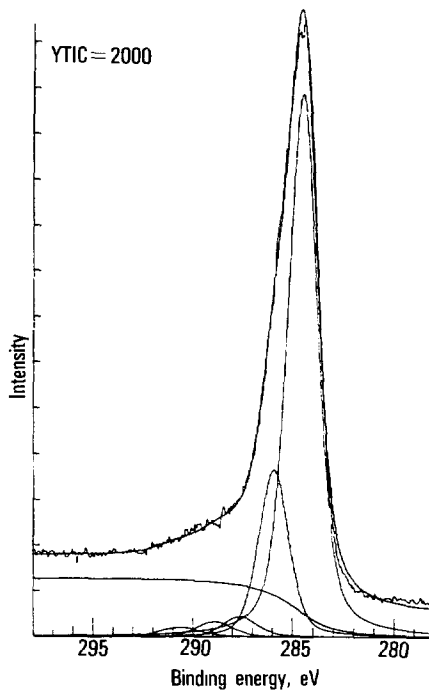


Fig. 10. Deconvolution of carbon spectrum of sample F3T.

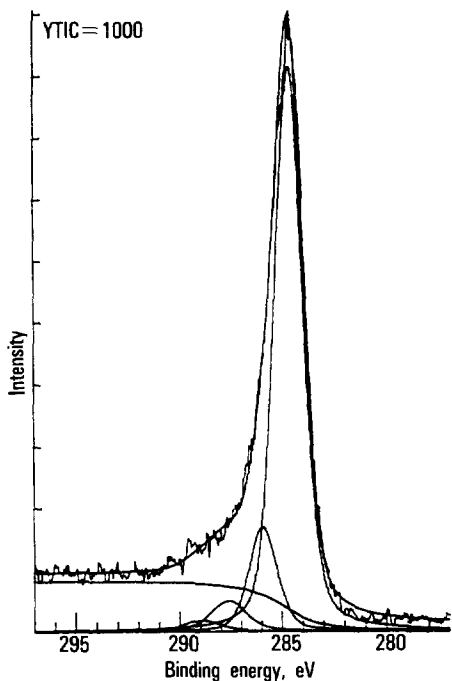


Fig. 9. Deconvolution of carbon spectrum of sample AS4/ER.

highly polar carboxylic acid. The ether type oxygen of AS4/H decreased by about 50% as compared to AS4, while the other types of oxygen of the sample AS4/H did not change much. This result also supports the peak shift of C_{1s} toward lower binding energy, as shown in Fig. 4, because the C-C bonding has a lower binding energy than the C-O bonding. All types of oxides of sample AS4/EO increased with an exceptionally large increase in carboxylic type oxygen, which is shown as a large shoulder at the high binding energy side. On the other hand, oxide groups of sample AS4/ER decreased with a large reduction in ether type oxygen.

Deconvolution results of the O_{1s} spectra of samples AS4 and AS4/H are illustrated in Fig. 11 and 12; two large peaks correspond to carbonyl oxygen (I) and hydroxyl or ether type oxygen (II), the former having lower binding energy and a small peak (III) at the highest binding energy is related to adsorbed oxygen or hydrocarbon con-

tamination.⁷ Fig. 11 shows two main peaks and a very small amount of physically adsorbed oxygen in sample AS4. Sample AS4/H has a negligible amount of adsorbed oxygen and shows much reduced intensity of ether type oxygen (Fig. 12). The deconvolution results of the oxygen spectra confirm the following:

1. Little adsorbed oxygen is present on the fiber surfaces.

2. The reduction in oxygen functional groups in sample AS4/H was due to the conversion of the C-O bond to a C-C bond rather than due to the removal of adsorbed oxygen.

The peak areas are listed in Table 4 along with

curve fitting parameters.

Depth Profiling

In order to probe the structure of carbon fibers as a function of distance from the surface, sputtering experiments were conducted. All the experimental parameters were fixed except for the sputtering time.

The effect of etching time on the carbon and oxygen spectra of AS4 fibers is shown in Fig. 13 and 14, and the changes in O/C ratio are summarized in Table 5. The intensities of C_{1s} spectra were so high that the changes in intensity are not distinguishable (Fig. 13), while the decrease in oxygen content is well represented in Fig. 14. The

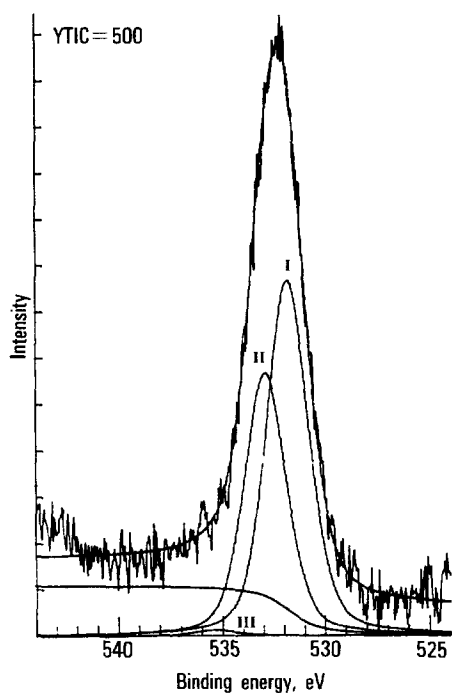


Fig. 11. Deconvolution of oxygen spectrum of sample AS4.

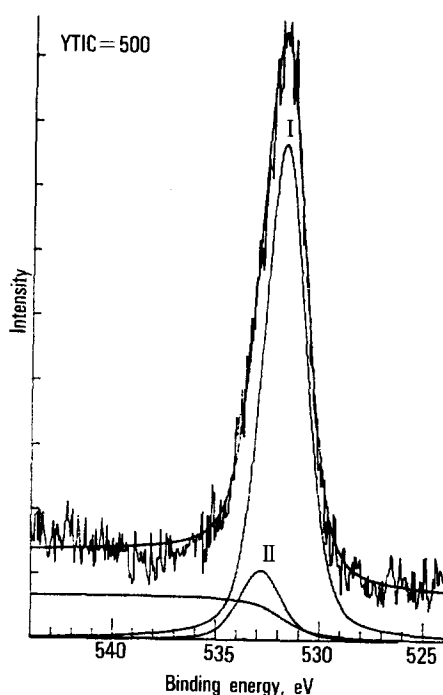


Fig. 12. Deconvolution of oxygen spectrum of sample AS4/H.

Table 4. Results of Curve Deconvolution of O_{1s} Spectra

Sample	Binding Energy, eV			FWHM (eV)	Area Ratio		
	I	II	III		I	II	III
AS4	531.75	532.84	535.43	2.4	56.9	42.2	0.9
AS4/H	531.75	532.84	535.43	2.4	87.7	12.3	0.0

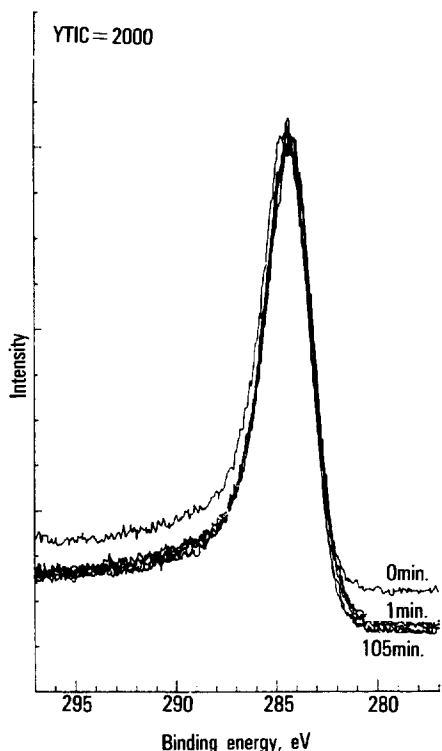


Fig. 13. The effect of etching time on carbon peak of AS4.

Table 5. Concentration Change of C_{1s} and O_{1s} along Depth of AS4 Fibers

Sputtering Time, min.	O_{1s}/C_{1s}	Scan Number
0	0.189	20
1	0.172	20
3	0.172	20
24	0.065	20
60	0.042	20
105	0.039	20

intensity of O_{1s} remains almost constant until 3 min. and then decreases remarkably after 24 min., losing 80% of its intensity. After 24 min., the intensity decreases slowly and then remains fairly constant after 60 min. Ishitani also found that 70% of the O_{1s} intensity was lost after 30 min. etching of the oxidized fibers.⁵ This result shows that a thin oxide layer is present on the fiber surface only.

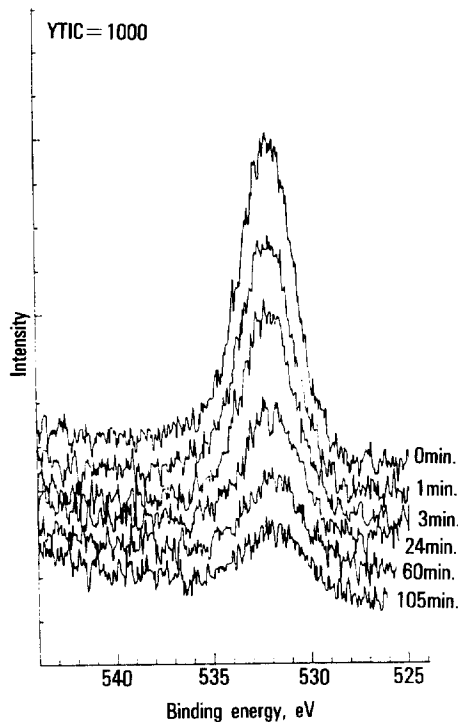


Fig. 14. The effect of etching time on oxygen peak of AS4.

CONCLUSION

X-ray photoelectron spectroscopy was very sensitive to detecting trace amounts of surface elements in addition to carbon and oxygen. Elemental analysis and sputtering experiments on AS4 fibers showed that a significant amount of oxygen (15%) is present on the fiber surfaces only. The deconvolution of the carbon peaks indicated that oxygen functional groups on the AS4 fibers consist of 67% hydroxyl or ether type oxygen, 20% carbonyl type oxygen, and 11% carboxylic acid. Also, deconvolution of oxygen spectra revealed that little adsorbed oxygen is present on the fiber surfaces.

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Graphite Fiber Surface Analysis Using X-ray Photoelectron Spectroscopy

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