

Effect of Microwave Nitrogen Plasma Treatment on Nicalon Fibers

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X-ray photoelectron spectroscopy and Auger electron spectroscopy were used to study the surface chemical changes that occur on Nicalon yarn treated with nitrogen plasmas. In all cases the plasma introduced new functionalities on the surface such as C-N, Si-O-N, and Si-N groups. The extent of nitridation increased with an increase in applied microwave power. Surface functionality changes were also readily detected by XPS valence-band spectra. No fiber damage was detected by electron spectroscopy. No degradation in tensile strength was also observed among the surface-treated fibers. Nitrogen plasma treatment of fibers proves to be an effective pretreatment of SiC fibers. The nitrided layer may serve to protect the fiber (diffusion barrier) during composite synthesis, or the surface functional groups newly introduced may serve as reaction or nucleation sites for further chemical vapor deposition processes.

Introduction

Ceramic fibers from polymer precursors, such as Nicalon SiC fibers (Nippon Carbon Co., Japan) produced by pyrolysis of poly(carbosilane) polymer, have been shown to have defect-controlled room-temperature strength properties.¹ Microstructural effects are also known to play a role in tensile strength and other mechanical properties although this role was shown¹ to be less important compared to the role of flaws in the case of the room temperature tensile strength properties. Studies²⁻⁴ have been carried out to investigate the thermal degradation of SiC fibers. There have also been recent reports on the effects of RF glow discharge plasma on the surface chemistry of this ceramic fiber.⁵ Information from such studies is especially useful in plasma-enhanced chemical vapor deposition (CVD) of these ceramic fibers where it is necessary to distinguish changes in mechanical properties (such as tensile strength, modulus, etc), if any, due to the plasma process from matrix-fiber interfacial chemistry.

Emphasis in the present study has been focused on the structural characterization of fibers and chemical state of surface species that have undergone nitrogen microwave plasma treatment. Specifically, spectroscopic techniques employed in this study include X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and scanning electron microscopy. The microstructure and chemical structure must be considered for characterization studies aimed at understanding the behavior of ceramic fibers exposed to plasma treatments. Microstructural studies address changes in the nature of the bulk fiber structure. Chemical structure studies provide information regarding the nature and the changes of the chemical species present as a function of surface treatment history.

Experimental Section

Commercially available Nicalon fibers (Nippon Carbon Co.) were used in this study. Attempts were made to remove the poly(vinyl acetate) sizing of the fibers by dip washing in acetone

for 3 min at room temperature, repeated twice with fresh acetone. However, it was difficult to remove the sizing completely by acetone wash as reported by other workers as well.⁶ The plasma treatment was carried out with an OPTHOS microwave power generator (Model MPG-4) and a McCarroll cavity. The Nicalon yarn was placed inside a quartz tube of inner diameter of 9 mm. The tube was then mounted in the cavity and connected to the vacuum line by Cajon ultraTorr fittings. The tube was evacuated to 0.01 Torr, and argon gas was let into the tube. The gas pressure was adjusted to a pressure of 0.1 Torr. The microwave generator was then turned on and an argon plasma was started in a region of the quartz tube away from the Nicalon yarn. Nitrogen gas was slowly and carefully let into the quartz tube until the characteristic pink color of the nitrogen plasma was observed. The argon gas flow was then turned off slowly, and the cavity was moved to the position of the Nicalon yarn. The sample treatments carried out are summarized in Table I. The nitrogen gas pressure within the quartz tube was kept at 0.1 Torr during the experiment. After the plasma treatment, the sample was passivated by nitrogen gas flow for 3 h before being studied by XPS or AES techniques. Sample handling and preparation for XPS and AES studies have been discussed elsewhere.⁷

Photoelectron spectroscopy measurements were carried out using a Physical Electronics PHI 5300 X-ray photoelectron spectrometer, using monochromatic Al K α X-radiation. The power was 600 W (15 keV, 40 mA). The base pressure in the sample chamber was 3×10^{-9} Torr. The spectrometer is also equipped with an electron flood gun that provides a low flux of electrons to compensate for sample charging. Low-resolution broad scans were collected at a pass energy of 178.9 eV in order to survey the elemental composition found over the entire XPS

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Table I. Sample Descriptions

sample	plasma gas	treatment time, min	forward power, W	reflected power, W	gas press., Torr	descriptions
a	none	0	0	0	≤0.1	acetone-washed fibers
b	nitrogen	10	10	0-1	≤0.1	plasma-treated fibers
c	nitrogen	10	20	0-1	≤0.1	plasma-treated fibers
d	nitrogen	10	30	0-1	≤0.1	plasma-treated fibers
e	nitrogen	10	40	0-1	≤0.1	plasma-treated fibers
f	nitrogen	10	50	0-1	≤0.1	plasma-treated fibers

energy range. High-resolution spectra were collected at a pass energy of 17.9 eV to obtain more detailed chemical information of the fiber surface. Valence-band spectra were collected at a pass energy of 8.95 eV. Calibration was based upon the C(1s) photoelectron peak of adventitious carbon at 284.6 eV.

The AES spectra were obtained with a Physical Electronics PHI 610 scanning Auger spectrometer with a base pressure of 5×10^{-9} Torr. The spectrometer is equipped with a single-pass cylindrical mirror analyzer (CMA) with a coaxial electron gun. Auger spectra were recorded with an energy resolution of 0.6%. Surface compositions were analyzed in the as-received state and after different sputtering times at 3-keV primary electron energy and with a 50-nA beam current.

Composition depth profiles of the near surface layers were obtained in the AES analysis. The spectra were collected after sputtering with a differentially pumped ion gun employing argon as the sputtering gas. AES depth profiles were obtained by using a 3-keV Ar⁺ ion beam rastered over an area of 2 mm × 2 mm. Under these conditions the sputtering rate for SiO₂ was 50 Å min⁻¹.

XPS and AES data analyses and manipulations were carried out using built-in software by Physical Electronics and have been described in detail elsewhere.⁷

Tensile strength of the Nicalon yarns was measured at room temperature with an Instron testing machine. A gauge length of 1 in. and a cross-head speed of 0.02 in./min were used. At least 20 measurements were made for each plasma treatment, and the average breaking load is reported.

Electron micrographs of the treated fibers were taken by using an AMRAY 1810 D scanning electron microscope. The treated fibers were mounted with carbon paste on aluminum stubs.

Results

Auger Electron Spectroscopy. The surface of the untreated fiber shows a large predominance of O and C over Si, as can be seen in Figure 1a. A survey scan of the untreated fiber from different lengths of the fiber tow show only a very low amount (<2 atom %) of surface nitrogen. On treating the acetone-washed fibers with nitrogen plasma results in a substantial increase in surface nitrogen content (12–30 atom %). This can be seen in Figure 1b, which shows a representative survey scan of a fiber treated with nitrogen microwave plasma at a power of 20 W. The AES depth profiles of the various treated fibers are shown in Figure 2.

In the present study, AES results were not used to determine bonding/chemical state information due to argon ion beam and electron beam generated surface damage and the artifacts they can generate in the AES spectra.^{8–10} X-ray photoelectron spectroscopy, which is a less destructive surface technique, was instead employed to obtain chemical information of the Nicalon fiber surfaces.

X-ray Photoelectron Spectroscopy. Survey Region. The low-resolution X-ray photoelectron survey spectra of the untreated Nicalon fiber and those of the nitrogen plasma treated fiber are shown in Figure 3. The survey spectra of the acetone-washed untreated Nicalon yarn as

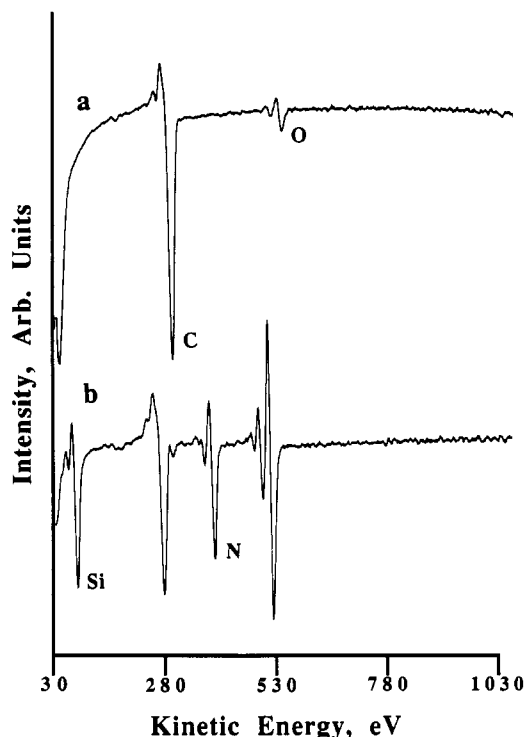


Figure 1. Low-resolution AES survey scans of (a) untreated Nicalon fiber and (b) nitrogen plasma treated Nicalon fiber. The particular fiber was treated with a 20-W nitrogen microwave plasma. The other fibers treated at various different microwave powers show survey scans similar to that of (b).

well as the nitrogen plasma treated fibers show only the elements silicon, carbon, nitrogen, and oxygen. No other elements were found on the fiber surface. The N(1s) peak was readily detectable for all the nitrogen plasma treated fibers but is almost undetectable in the untreated fiber. The survey scan of the untreated sample shows only a weak Si(2p) signal and strong O(1s) and C(1s) signals. Nitrogen plasma treated fibers show strong N(1s) and Si(2p) signals, and the relative intensity of the C(1s) signal is decreased. The relative signal intensities of the N(1s) and Si(2p) increases with an increase in the forward power of the nitrogen plasma up to a maximum applied power of 50 W.

Si(2p) Region. The Si(2p) spectrum of the acetone-washed fiber and the plasma-treated fiber may be resolved into three peaks with binding energies of about 101.3, 102.5, and 103.4 eV. A representative curve-fitted spectrum is shown in Figure 4a. According to Raider and co-workers,¹¹ the Si(2p) line in SiO₂ occurs at 103.5 eV, whereas Si₃N₄ has the Si(2p) line at 101.4–101.7 eV. In addition, a number of nonstoichiometric silicon oxynitrides produce a single Si(2p) peak between 101.7 and 103.0 eV. We thus assign peak 1 to Si in Si_xN_y and SiC, peak 2 to silicon oxynitride and SiO_x species, and peak 3 to SiO₂.

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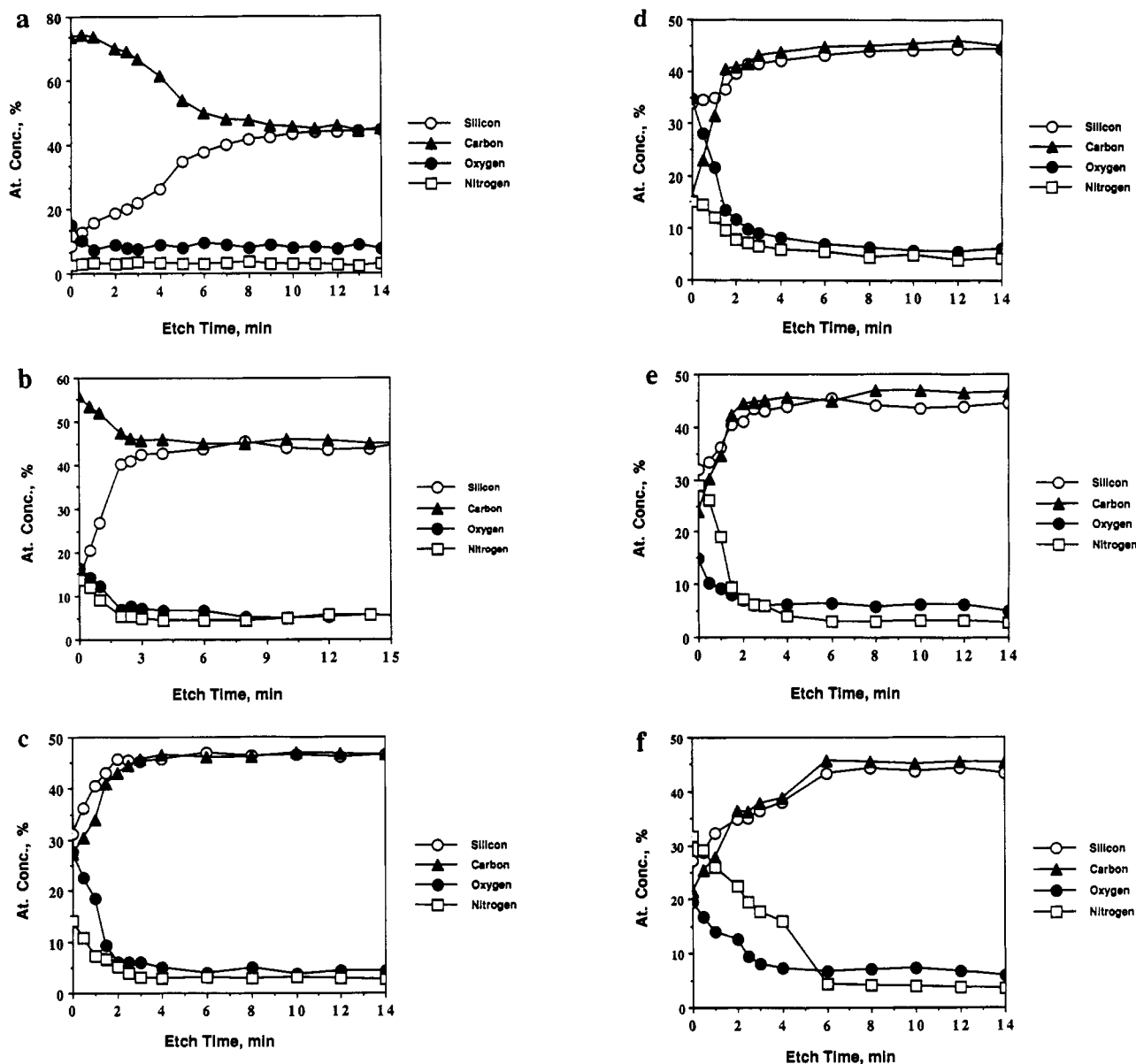


Figure 2. Auger depth profiles of the nitrogen plasma treated fibers at various microwave powers: (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 W.

Table II. Si(2p) Peak Positions, Relative Peak Areas, and Peak Area Ratios as a Function of Microwave Power

microwave power, W	peak one		peak two		peak three		peak 1:peak 2 area ratio	peak 1:peak 3 area ratio
	BE, eV	area, %	BE, eV	area, %	BE, eV	area, %		
0	101.2	4.79	102.5	68.01	103.7	27.2	0.07	0.18
10	101.2	24.03	102.2	35.58	103.2	40.39	0.68	0.59
20	101.4	30.71	102.4	53.46	103.4	15.83	0.57	1.94
30	101.1	36.21	102.3	43.73	103.5	20.06	0.83	1.81
40	101.6	82.57	102.9	17.43			4.74	
50	101.7	83.33	102.8	16.67			5.00	

Table II summarizes the Si(2p) peak positions and relative peak areas of the acetone-washed and plasma-treated fibers. Note that peak 3 disappears at applied plasma powers of ≥ 40 W.

O(1s) Region. The O(1s) spectra for the untreated fibers and those treated with a 50-W nitrogen plasma were fitted to three peaks, while those of the rest of the surface-treated fibers could only be fitted to two peaks (Figure 4b). The peak at 532.2 eV is assigned to oxygen in a Si-O-Si environment,¹²⁻¹⁴ carboxyl (COOH) type oxygen,

Si-O-N oxygen,¹⁵ and oxygen in the ether (C-O-C) group,¹² and the peak at 533.0 eV is assigned to a hydroxide species (Si-OH)¹⁶ and an alcohol (C-OH) species.¹² The third peak with a binding energy of 534.9 eV is assigned to adsorbed oxygen and water. The O(1s) component peak

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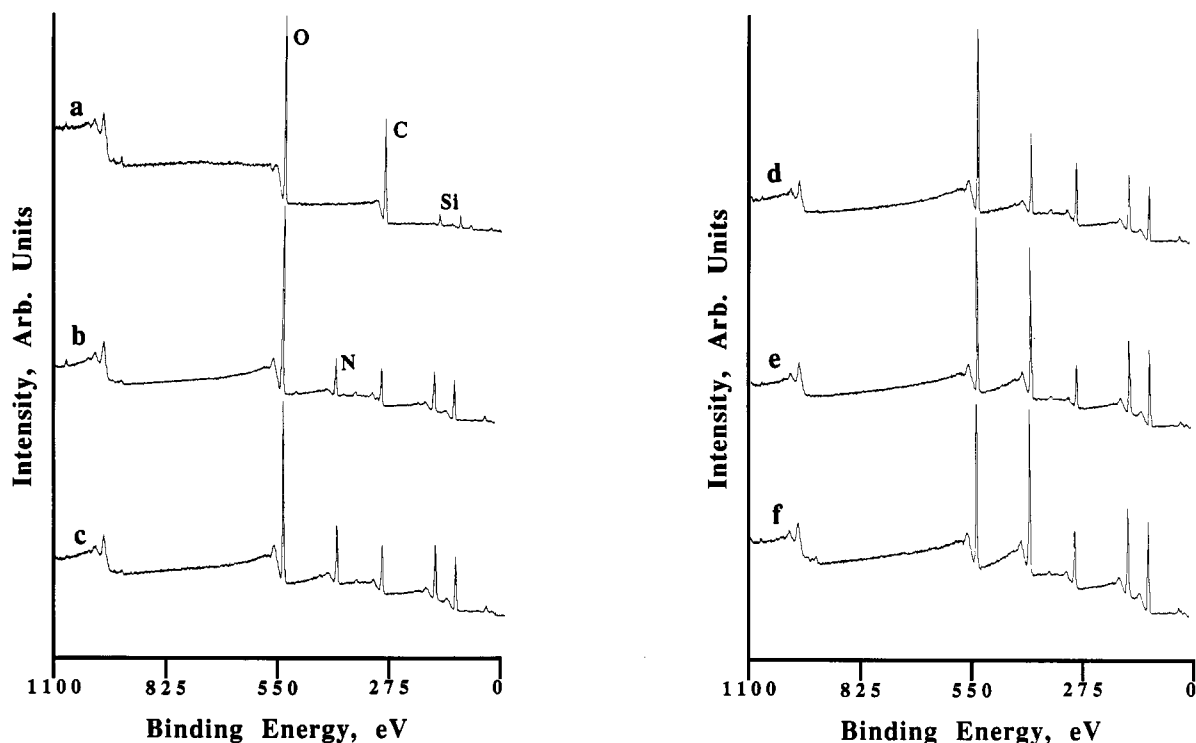


Figure 3. Overall X-ray photoelectron spectra of the Nicalon fibers treated at various microwave powers: (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 W.

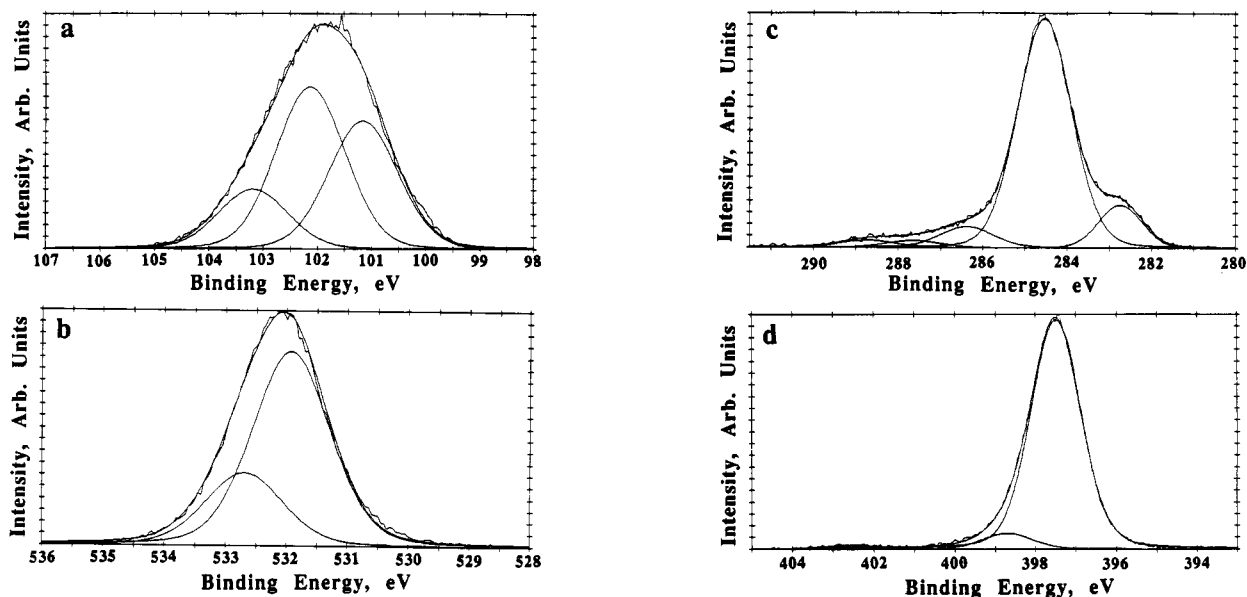


Figure 4. Representative curve-fitted X-ray photoelectron spectra for the nitrogen plasma treated Nicalon fibers. The forward microwave power applied was 10 W. The spectra are shown with different intensity scales, the scales being chosen to represent the difference between the maximum and minimum points in the data: (a) Si(2p), (b) O(1s), (c) C(1s), and (d) N(1s).

positions and the peak area percentages are summarized in Table III.

C(1s) Region. As shown in Figure 4c, the C(1s) spectra were fitted to five peaks, namely, a "carbide" peak at 282.9 eV (peak 1), a main "graphitic" peak at 284.6 eV (peak 2), and three "oxide" peaks (peaks 3–5). The "oxide" peaks denoted as peaks 3–5 are shifted 1.5–1.9, 2.8–3.3, and 4.2–4.5 eV from the main "graphitic" peak, respectively. Peak 3 is associated with the carbon atom in alcohol (C–OH) groups, ether (C–O–C) groups, and C=N groups.^{2,17} Peak 4 corresponds to the carbon atom in carbonyl (C=O) type groups,¹⁷ and peak 5 is that of carbon in carboxyl

Table III. O(1s) Peak Positions and Relative Peak Areas as a Function of Microwave Power

micro-wave power, W	peak one (C=O, Si-O-Si)		peak two (SiOH, C-O-C, C-OH)		peak three	
	BE, eV	area, %	BE, eV	area, %	BE, eV	area, %
0	532.1	56.32	533.4	32.7	534.6	10.99
10	532.3	66.61	533.1	25.88		
20	532.2	84.1	532.9	15.91		
30	532	72.83	532.8	27.17		
40	532.1	76.74	532.8	23.26		
50	532.1	80.52	533	15.83	534.9	3.65

(COOH) or ester (COOR) type groups.^{2,17} The C(1s) component peak positions and peak area percentages for the C(1s) spectra are summarized in Table IV.

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Table IV. C(1s) Peak Positions and Relative Peak Areas for Various Microwave Power Settings

microwave power, W	peak one (C-Si)		peak two (C-C)		peak three (>C-O-R, C-N)		peak for (>C=O)		peak five (COOR)		total oxide area (3 + 4 + 5)
	BE, eV	area, %	BE, eV	area, %	BE, eV	area, %	BE, eV	area, %	BE, eV	area, %	
0	282.9	1.37	284.6	49.42	286.3	28.86	287.2	5.4	288.7	13.91	48.17
10	283	18.2	284.6	68.35	286.5	9.2	287.8	1.52	289	2.73	13.45
20	282.8	10.93	284.6	77.36	286.5	7	287.7	2.28	288.8	2.44	11.72
30	283	12.03	284.6	70.88	286.4	10.11	287.9	3.44	289.1	3.54	17.09
40	282.9	11.93	284.6	68.69	286.3	10.32	287.6	4.59	289	4.47	19.38
50	283	11.86	284.6	65.64	286.2	11.55	287.4	6.95	288.8	3.99	22.49

Table V. N(1s) Peak Positions, Relative Peak Areas, and Peak Area Ratios at Various Microwave Powers^a

microwave power, W	peak one (N-Si)		peak two (group A)		peak three (group B)		peak 2:peak 1 ratio	peak 3:peak 1 ratio
	BE, eV	area, %	BE, eV	area, %	BE, eV	area, %		
10	397.6	92.72	298.8	6.35	402.7	0.92	0.07	0.01
20	397.8	92.32	398.9	6.48	402.5	1.2	0.07	0.01
30	397.7	88.9	399	6.49	402.7	4.61	0.07	0.05
40	397.5	88.41	398.5	7.47	402.6	4.13	0.08	0.05
50	397.5	87.17	398.5	6.8	402.6	6.02	0.08	0.07

^aData for the untreated fiber are not reported due to the low signal-to-noise ratio obtained.

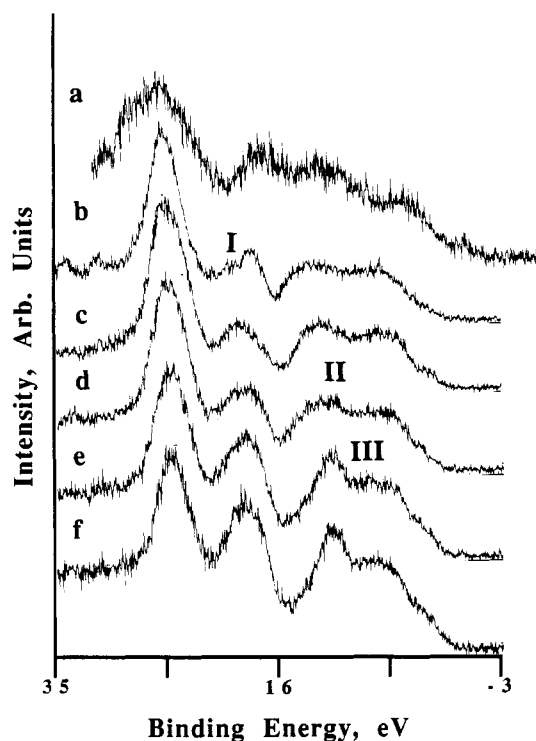


Figure 5. Valence-band XPS spectra of the various Nicalon fiber samples treated at the various microwave powers: (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 W.

N(1s) Region. The N(1s) envelope maximum occurs at 397.6 eV. This is in agreement with the binding energy quoted for thermally grown Si₃N₄ films.¹⁸ The N(1s) spectra are fitted to three peaks as shown in Figure 4d. Peak 1 is assigned to N-Si₃ species,¹² and peak 2 is assigned to carbon-bonded nitrogen species as those described in ref 12. Peak 3 arises from C-N-O species.¹⁹ The N(1s) component peak positions, peak area percentages, and the area ratios of peak 2/peak 1 and peak 3/peak 1 for the various treated fibers are summarized in Table V.

Valence-Band Spectra. The valence-band region is a useful probe of surface chemical changes,^{17,20} even more

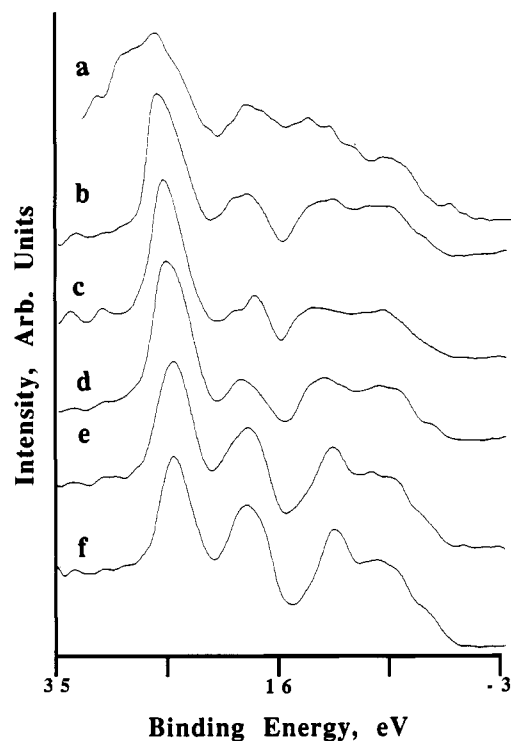


Figure 6. Smoothed valence-band XPS spectra of the various Nicalon fiber samples treated at the various microwave powers: (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 W.

Table VI. Tensile Strength Measurements^a for As-Received and Plasma-Treated Fibers

sample	microwave power, W	tensile strength, ^b lb
untreated fiber	0	30.4 ± 2.7
treated fiber	30	28.7 ± 3.1
treated fiber	50	29.5 ± 3.5

^aTensile strengths of 20 samples were taken for each plasma treatment. ^bBreaking load.

sensitive to chemical changes than are the core regions. Figure 5 shows the valence band spectra of samples a-f. The smoothed spectra and the second-derivative spectra of the valence-band spectra of these samples are shown in Figures 6 and 7, respectively.

Tensile Strength and Microstructural Studies. As shown in Table VI, the nitrogen plasma treated fibers did

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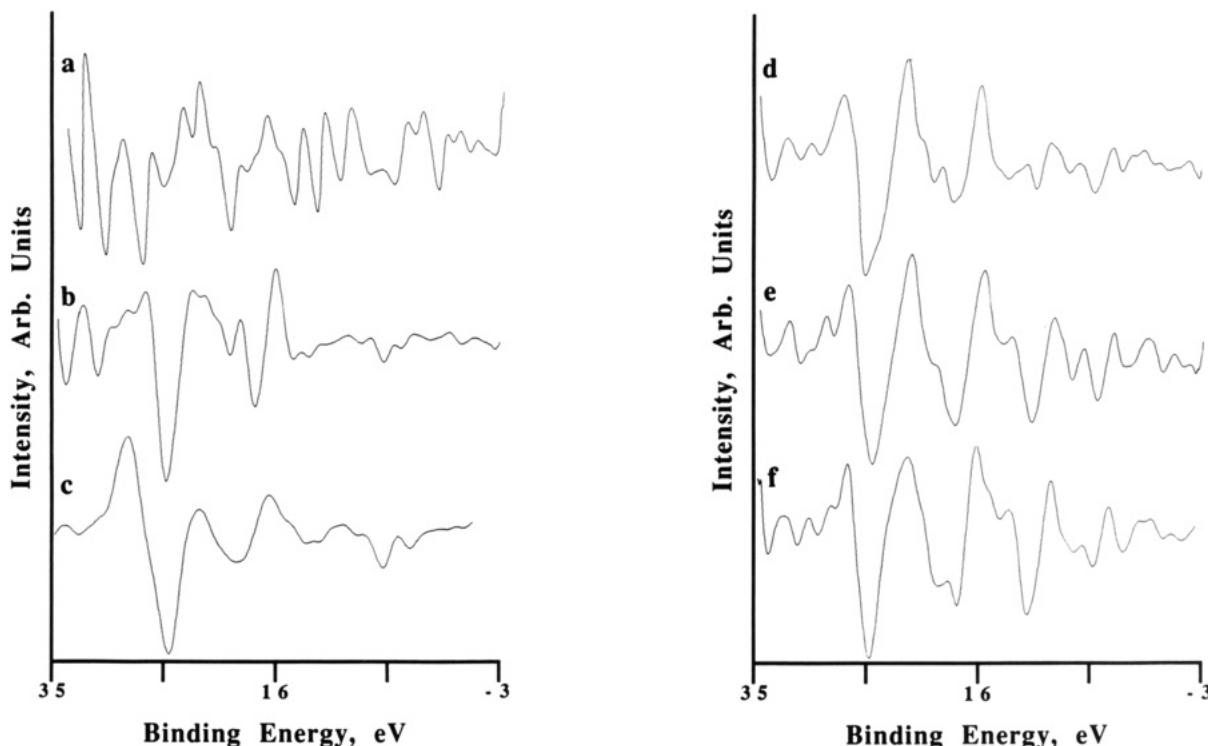


Figure 7. Second-derivative spectra of the smoothed valence-band XPS spectra of the various Nicalon fiber samples treated at the various microwave powers: (a) 0, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50 W.

not show any loss in tensile strength. Examination of the treated fibers using the scanning electron microscope revealed that the surfaces of the fibers were smooth. No flaws or pitting of the surfaces were observed. Figure 8 shows representative micrographs of fibers treated with a microwave nitrogen plasma at 30 and 50 W.

Discussion

Auger Electron Spectroscopy. The Auger sputter depth profile (Figure 2a) for acetone-washed untreated sample surface is composed predominantly of carbon, which is consistent with the presence of solvent residue or from remnants of the organic sizing on the fiber. A small amount of the silicon (7%) on the as-received sample indicates there is an uneven coating, as has been observed by other workers.^{21,22}

Treatment of the fiber with a 10-W nitrogen plasma results in the removal of a substantial amount of surface carbon. This is evident in the Auger sputter depth profile (Figure 2b), which shows a much lower surface carbon level when compared to the untreated fibers (55% vs 72%) and that this surface carbon layer is removed after a shorter argon ion sputter time (3 min total sputter time as compared to 6 min). A short argon ion etch of 2 min results in a rapid decrease in the atomic concentration of C, which is accompanied by a parallel decrease in N and O. This suggests that the nitrated layer formed at 10-W microwave power is extremely thin (~ 150 Å).

Treatment of the fibers with a 20-W nitrogen plasma results in the carbonaceous overlayer being removed, exposing the fiber surface. The relative atomic concentration (rac) of C falls below that of Si (Figure 2c). The surface of the fibers is Si rich, and there is also an increase in the amount of surface oxygen (from about 18 atom % to about

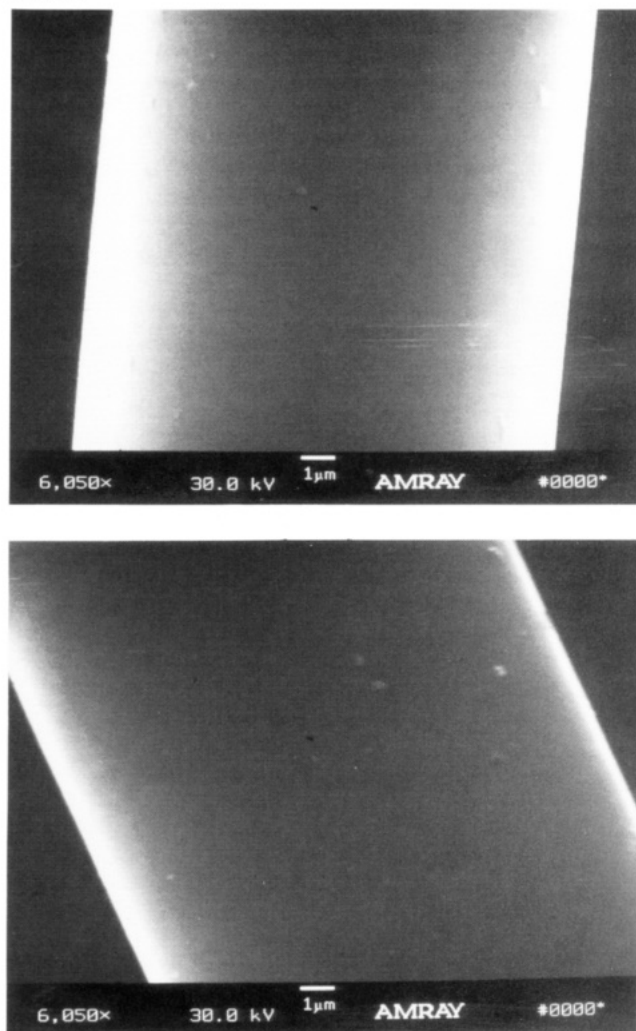


Figure 8. Scanning electron micrographs showing the surface morphology of nitrogen plasma treated fibers at (a) 30 and (b) 50 W.

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28 atom %), suggesting an overlayer of SiO₂ in the 20-W plasma-treated fibers. These results are in agreement with data of Simon and Bunsell.²³ They showed the fiber surface is composed of a thin coat of SiO₂. The rac and penetration depth of N remain unchanged from that of the 10-W plasma treatment.

The Auger sputter depth profile of 30-W nitrogen plasma treated fibers (Figure 2d) shows the carbonaceous overlayer is completely removed, exposing the silicon dioxide surface layer of the fiber. This accounts for the relative high amount (35%) of surface oxygen. As with the case of the 10- and 20-W plasma-treated fibers, the relative atomic concentration of the surface nitrogen is about 15 atom %. The nitrated layer is thin (~150 Å), being etched away after about 3 min of argon ion sputtering.

There is a large increase in the rac of surface nitrogen (from 15 to 30 atom %), accompanied by a decrease in the amount of surface O when the fibers were treated with a 40-W nitrogen plasma (Figure 2e). This suggests that the SiO₂ surface layer reacted with the nitrogen plasma resulting in loss of oxygen. However, the penetration depth of the N remains unchanged, being about 150 Å. Significant changes are observed on treating with a 50-W microwave plasma (Figure 2f). The surface amount of N remains about 30 atomic %, but the penetration depth increased by a factor of about 2 (increasing to 6 min of sputter time, approximately 300 Å deep). Thus at 50-W microwave power, the N is implanted deeper into the fiber.

To summarize, the present AES study shows that the surface microwave nitrogen plasma treatment is a function of applied microwave power. At 10 W a large fraction of the organic residue is removed. The layer of organic is completely removed at 30-W power. A 40-W microwave power causes both the removal of the solvent residue as well as an increase in surface nitrogen. At 50-W power, nitrogen implantation into the fiber is effected.

The nitrogen introduced during microwave plasma treatment may be associated with C and/or Si. To obtain chemical information on the surface species formed on nitrogen microwave plasma treatment, we now turn to the XPS data.

X-ray Photoelectron Spectroscopy. Valence Band Spectra. All samples show a strong O(2s) feature at a binding energy of around 25 eV. The O(2s) region of the untreated sample contains a number of features and is much broader than that of the nitrogen plasma treated fibers. Around 20 eV, the C(2s) and N(2s) features overlap. We have identified the features of the valence band with the help of refs 17, 19, 24, and 25. The Si(3p) electrons contribute to a 4-eV-wide peak at the top of the valence-band spectrum, and the Si(3s)-derived states are responsible for the "hump" between 5 and 15 eV. The carbon contributes to the characteristic three-band structure. A wide band is located between 16 and 21 eV that is mainly composed of the C(2s)-derived states, and a second narrower, less intense peak is located at about 10–15 eV containing a strong mixture of C(2s) and C(2p) character. The C(2p) state gives rise to a weak structure extending

from about 10 eV to the top of the valence band.

Treatment of the Nicalon fiber with nitrogen plasma results in the narrowing of the O(2s) peak and the appearance of the characteristic N bands. The most prominent N band is centered at 20 eV, which has almost exclusively N(2s) character (peak I). Other N bands overlap with those of the C and Si bands, namely, the N(2p_{x,y}) bands giving rise to bands at 12.4 eV (peak II) and 7.5 eV (peak III). The nonbonding N(2p_z) lone pair gives rise to a broad peak at 4.9 eV (the contribution from N(2p_{x,y}) states in the region is less than 20%). The appearance and growth of these N bands are more easily seen in the second-derivative spectra.

Another prominent change in the valence-band spectrum is a substantial decrease in the intensity of the C(2s) and C(2p) bands. A further increase in the applied microwave power results in a steady increase in the intensity of the N bands. These trends were also observed in the core level photoelectron peaks. When a microwave power of ≥40 W was applied, the N(2s) and N(2p_{x,y}) bands substantially increase in intensity.

Si(2p) Region. Table II shows that the Si(2p) spectrum of the samples can be fitted to two or three peaks. The trends observed in the peak areas of peak 1 (Si–N and Si–C functionalities), peak 2 (Si–O–N functionality), and peak 3 (Si–O functionality) suggest that at low microwave powers (10–20 W), the Si–O–Si bonds of the surface SiO₂ are broken by the active N species, preferentially forming Si–O–N bonds over complete disruption of the Si–O bonds to form Si–N. This is indicated by the decrease in the peak area of peak 3 to about 40% at 10 W and a further decrease to 17% at 20- and 30-W powers. This decreasing trend in the area of peak 3 is accompanied by an increase in area of peak 2 which goes through a maximum at a power of 20 W. Between 20 and 30 W, any additional Si–N is formed at the expense of the previously formed Si–O–N species. Thus, the relative peak area of peak 3 remains unchanged while a slight decrease in the relative area of peak 2 is observed at 30 W.

The increase in relative area of peak 1 is small (~12%) between powers of 10 and 30 W. This suggests that at 20–30 W the kinetic energy of the active N species in the plasma is not large enough to penetrate deep into the fresh SiO₂ layer to form more nitride/oxynitride species. Thus increasing the power to 30 W results only in the formation of a small addition of nitride from the already formed oxynitride layer. This accounts for the small increase in the amount of the nitride accompanied by a slight decrease in the amount of oxynitride with no apparent change in the amount of Si–O functionality. This observation is in agreement with the Auger results which showed no difference in the N depth profile between the 20- and 30-W plasma-treated samples.

At a microwave power of ≥40 W, the N species possess enough kinetic energy to react with the deeper layers of SiO₂ to form additional nitrides and oxynitrides. However, the energy of the activated N species in the plasma have sufficient energy to completely break the Si–O–Si bonds, resulting in larger amounts of nitride formed over oxynitride. This is observed as a dramatic increase in the area of peak 1 (from 36% to 82.5%) at ≥40 W accompanied by a sharp decline in the area of peak 2 and the disappearance of peak 3 from the Si(2p) envelope. Thus at powers ≥40 W the SiO₂ surface layer is probably entirely disrupted by the N plasma. Although peak 1 accounts for the total amount of Si–C and Si–N species, we noted in Table IV that an increase in microwave power above 20 W did not change the peak area of the Si–C species. Thus, any in-

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Table VII
(A) Component O(1s), N(1s), and C(1s) Peak Areas Expressed as an Atomic Ratio of the Total Si(2p) Peak

microwave power, W	O(1s)/total Si(2p)			N(1s)/total Si(2p)			C(1s)/total Si(2p)				
	peak 1	peak 2	peak 3	peak 1	peak 2	peak 3	peak 1	peak 2	peak 3	peak 4	peak 5
10	0.86	0.33	0.00	0.58	0.04	0.01	0.12	0.46	0.06	0.01	0.02
20	0.82	0.15	0	0.41	0.03	0.01	0.09	0.61	0.06	0.02	0.02
30	0.54	0.20	0	0.46	0.03	0.02	0.07	0.41	0.06	0.02	0.02
40	0.52	0.16	0	0.79	0.07	0.04	0.06	0.36	0.05	0.02	0.02
50	0.49	0.10	0.02	0.86	0.07	0.06	0.07	0.39	0.07	0.04	0.02

(B) Component O(1s) and N(1s) Peak Areas Expressed as an Atomic Ratio of the Total C(1s) Peak

microwave power, W	O(1s)/total C(1s)			N(1s)/total C(1s)			Si(2p)/total C(1s)		
	peak 1	peak 2	peak 3	peak 1	peak 2	peak 3	peak 1	peak 2	peak 3
10	1.29	0.50		0.87	0.06	0.01	0.36	0.53	0.61
20	1.03	0.19		0.52	0.04	0.01	0.39	0.67	0.20
30	0.94	0.35		0.79	0.06	0.04	0.63	0.76	0.35
40	1.01	0.31		1.52	0.13	0.07	1.59	0.34	0.00
50	0.83	0.16	0.04	1.46	0.11	0.10	1.42	0.28	0.00

Table VIII. Component O(1s), Si(2p), and C(1s) Peak Areas Expressed as an Atomic Ratio of the Total N(1s) Peak

microwave power, W	O(1s)/total N(1s)			Si(2p)/total N(1s)			C(1s)/total N(1s)				
	peak 1	peak 2	peak 3	peak 1	peak 2	peak 3	peak 1	peak 2	peak 3	peak 4	peak 5
0	1.38	0.54	0	0.39	0.57	0.65	0.19	0.73	0.10	0.02	0.03
20	1.84	0.35	0	0.69	1.21	0.35	0.20	1.39	0.13	0.04	0.04
30	1.06	0.40	0	0.71	0.85	0.39	0.14	0.80	0.11	0.04	0.04
40	0.58	0.18	0	0.92	0.19	0.00	0.07	0.40	0.06	0.03	0.03
50	0.50	0.10	0.02	0.84	0.17	0.00	0.07	0.39	0.07	0.04	0.02

crease in peak 1 in Table II is attributed to an increase in the amount of nitride (Si-N) formed. At microwave powers ≥ 20 W, most of the surface Si is associated with N in the form of nitrides and oxynitrides (Table V). At ≥ 40 W, the surface N is mainly associated with N as nitride.

O(1s) Region. While the as-received Nicalon fiber and the fiber treated with a 50-W nitrogen plasma show three types of surface oxygen, the other plasma-treated samples show the presence of only two types of oxygen peaks, with peak 2 (hydroxyl functionality) being the more prominent peak. The loss of peak 3 on plasma treatment of ≤ 40 W is expected as the surface adsorbed oxygen and water is removed by the nitrogen plasma. The reappearance of peak 3 in the sample treated with a 50-W plasma may be due to reaction of the surface-active sites, which may not have been completely passivated, with the atmosphere on transport to the spectrometer.

C(1s) Region. Table IV shows that the amount of oxide formed falls from peak 3 to peak 5. The total oxide area, which is also listed in Table IV, increases with increasing microwave power. The oxides may be formed due to a leak in the plasma line or by reacting with the atmosphere on transferring the fibers to the spectrometer. Another possible oxygen source can also be from the thin SiO₂ surface layer present on the SiC fiber. The main graphitic peak area ($BE_{C(1s)} = 284.6$ eV) decreases from about 77% to 66% with increasing applied microwave power. The relative peak area of the Si-C species (peak 1) decreased from 18% to 11% on increasing the power from 10 to 20 W. A further increase in the microwave power did not change the relative peak area of the Si-C species.

Among the carbon species associated with oxygen, the amount of -COOR groups does not vary much with plasma treatment, though a slight increase in the amount at high microwave power is observed. The -C=O peak area increased by 1-2% for every 10-W increase in microwave power. The relative peak area of peak 3 does not vary much with surface treatment.

N(1s) Region. Nitrogen plasma treatment of the fibers results in the incorporation of substantial amounts of N

into the fiber. This is evident by comparing the relative peak heights of the N(1s) and N(KLL) signals in the XPS and AES survey scans, respectively, of the acetone-washed untreated fibers with those of the plasma-treated ones. The results summarized in Table V for the N(1s) spectra of the nitrogen plasma treated fibers indicate that most of the N is tied up with the surface Si on the fiber rather than with the C and O for all applied microwave powers. This is reflected by peak 1 (Si-N functionality) accounting for most of the peak area of the N(1s) spectrum indicating that most of the N is tied up with the surface. Thus even at low microwave power (< 30 W), although there are substantial amounts of surface C (from AES depth profile results), the larger fraction of N is associated with Si rather than C. The results also show that the relative peak area of peak 2 (N-C functionality) is unaffected by the applied power. This is consistent with the relative peak area of peak 3 in the C(1s) (C-N and C=O functionalities) spectrum not being altered by the applied power.

Si(2p), O(1s), C(1s), and N(1s) Spectral Comparisons. The ratios of the area of each O(1s), N(1s), and Si(2p) peaks components to total C(1s) peak area for each sample are summarized in Table VIIA. The results for Table VIIA were used to calculate their respective atomic ratios, assuming a homogeneous sample and using the sensitivity factors obtained for the spectrometer. Table VIIB lists the calculated atomic ratios.

There is an initial decrease in the O/C atomic ratio when the power is increased from 10 to 20 W. For powers ≥ 20 W the O/C atomic ratio remains relatively unchanged until a power of 50 W is applied, in which case a drop in the O/C ratio is observed. The decrease in the O/C atomic ratio at 20 and 50 W is a combination effect of the removal of the surface oxygen by the N plasma as well as the depletion of the SiO₂ surface layer.

The XPS results suggest the formation of a Si₃N₄ overlayer from the reaction of the nitrogen plasma with the SiO₂ layer found on the Nicalon fiber surface. This is seen in Table VIIA, which summarizes the area ratios of the peak components of the Si(2p), O(1s), and N(1s) photoelectron peaks to the total C(1s) peak area. Both

peak atomic ratios of peak $1_{N(1s)}$ /total C(1s) and peak $1_{Si(2p)}$ /total C(1s) increases at powers ≥ 20 W, indicating an overall increase of Si_xN_y to SiC at the surface because peak 1 in both the N(1s) and Si(2p) envelopes corresponds to Si_xN_y species.

The formation of an overlayer Si_xN_y with increase in microwave power is also reflected in Table VIII, which summarizes the atomic ratios of the component peaks of the O(1s), Si(2p), and C(1s) spectra with respect to the total N(1s) peak. The decrease in the atomic ratio of peak $1_{C(1s)}$ (Si-C) to the total N(1s) peak is in agreement with the formation of an Si_xN_y layer over the SiC-based Nicalon fibers.

The decreases observed in the peak $1_{O(1s)}$ /total N(1s) and peak $2_{O(1s)}$ /total N(1s) atomic ratios are primarily due to the removal of surface oxygen species accompanied by an increase in amounts of nitride and oxynitride formed.

A survey of the surface morphology of the nitrogen plasma treated fibers at 6000 times magnification revealed that the fibers exhibit a smooth Si_xN_y sheath and the absence of flaws and pitting. Thus, the surface treatment did not cause degradation of the fiber surface. This explains the retention of the tensile strength of the fibers even after surface treatment. The surface of the fiber was not degraded even after a 50-W nitrogen plasma treatment. The AES depth profile together with the scanning electron micrographs suggest that the Si_xN_y sheath formed around the fiber grows uniformly in thickness at high microwave power (>40 W).

Conclusions

Microwave nitrogen plasma treatment has been used to effectively modify the surface of Nicalon fiber. At low microwave powers, the surface carbonaceous layer is removed with the formation of silicon nitride and oxynitride. Various functional groups were also introduced in small amounts by surface treatment. These surface groups include -C-OH, -C-O-C-, C=O, and -C-N functionalities. At higher microwave powers (≥ 40 W), the amount of surface Si_xN_y is increased substantially while amounts of the other surface nitrogen functional groups remain low. High microwave powers result in the complete reduction of the surface SiO_2 layer with the active N species as well as an increase in the nitrogen penetration depth into the fiber. Silicon nitride formation is favored over silicon oxynitride. The treatment affects only the surface chemistry, leaving the bulk structure unchanged.

The results of the present study suggest the potential use of microwave nitrogen plasma pretreatment to form a thin Si_xN_y surface layer without degradation of the tensile strength and surface morphology. This layer may be used as a barrier layer for further fiber processing of fiber coatings.

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Synthesis and Characterization of Poly[4-((*tert*-butoxycarbonyl)oxy)styrene-sulfone]

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Poly[4-((*tert*-butoxycarbonyl)oxy)styrene-sulfone] (TBSS) was synthesized by a thermally induced radical copolymerization of 4-((*tert*-butoxycarbonyl)oxy)styrene and sulfur dioxide using AIBN as the initiator. The effect of polymerization conditions such as temperature, monomer feed ratio, and monomer concentration on the copolymer molecular weight and composition was studied. The styrene-sulfone monomer sequence distribution was determined by NMR techniques, and the materials were found to be random copolymers of 4-((*tert*-butoxycarbonyl)oxy)styrene and SO_2 . The monomer triad sequence distribution was identical for copolymers of equivalent composition prepared by different synthetic routes. The onset temperature for the thermal deprotection reaction decreases somewhat with increased incorporation of SO_2 relative to the parent styrene polymer, while the T_g increases. For imaging applications, it was determined that the extent of *tert*-butoxycarbonyl removal at a given dose decreased with increasing SO_2 content; a phenomenon that was ascribed to differences in the catalytic chain length and diffusion distance of the photogenerated acid.

Introduction

The *tert*-butyl protecting group¹ has been used extensively for the synthesis of polymers with acid or phenol functionalities that might otherwise be elusive. More recently, such chemistry has allowed the development of systems in which the ester group is removed by a thermally

driven, catalytic reaction that is initiated by a photogenerated acid.²⁻⁴ One application of such chemistry is in the area of microlithography. Specifically, polymers such as poly((*tert*-butoxycarbonyl)oxy)styrene^{2,3} have been used

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