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Influence of Plasma Treatment on the Electroless Deposition of Copper on Carbon Fibers

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Air and nitrogen glow discharge were used to replace chromic acid pretreatment to deposit copper film on carbon fiber surfaces from an $CuSO_4$-HCHO electroless system. A greater copper uptake and a more uniformly coated copper film were obtained for plasma-treated carbon fibers. The adhesion between the copper film and the carbon fibers was also improved. An orthogonal table $L_9(3^4)$ was used to study the effects of discharge pressure, discharge power, time and gas type on the copper uptake. Scanning electron microscopy (SEM), reflection absorption infrared spectroscopy (RAIR) and X-ray photoelectron spectroscopy (XPS) at different depths were applied to characterize the physical and chemical changes of the surface of the carbon fibers. The results showed that after plasma treatment, the carbon fiber surface became rough and several types of polar oxygen groups, such as carboxylic acid COOH, esters COOC, quinones Ph=O, etc., were introduced into the carbon fiber surface. A mechanism of plasma treatment effects on copper electroless deposition on the carbon fiber surface is also suggested.

Keywords plasma treatment, carbon fibers, copper film deposition

Introduction

Carbon fibers are usually coated with a metal film before they can be put into practical use. In carbon fiber-metal matrix composites, they are coated with a layer of Cu, Ti-B or Si to prevent oxidation of the carbon fibers and metal-carbide formation at high melting temperatures or to get aluminum-carbon fiber composites with excellent mechanical properties (1–5). Carbon fiber-reinforced copper matrix composites are useful materials with high thermal conductivity for use in semiconductors (diodes and thyristors) and electrical contacts (6). Nickel-coated carbon fibers are used in polymer materials for enhancing the electrical conductivity and electromagnetic interference shielding (7). Capacitors with high specific energy density are made from active carbon fibers which are sprayed with an aluminum layer to be used for collecting electrodes (8). Carbon fibers with a metal layer are having increasing applications in advanced materials.

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There are many ways to deposit a layer of metal on the surface of materials, such as chemical vapor deposition (CVD), electroless deposition, electrochemical deposition, heat spray or plasma spray, etc (9–11). Among these coating methods, electroless deposition is extensively used because of its low cost, low operating temperature, easily controlled thickness, etc. It usually includes the following steps in its process: etching, etchant neutralizing, sensitizing, activating and metal deposition. Etching provides good adhesion of metal to the substrate materials by micro-roughening and chemically modifying the surface through oxidation with chromic acid or sulfuric acid solution. It is of critical importance for the performance of the composites, especially for carbon fibers with a smooth surface, containing 99% carbon and with non-polar groups (12). But because etching with chromic acid and sulfuric acid and the successive neutralization bring about the problem of contamination of the environment, some other environmentally-friendly methods are being developed to replace this etching step, such as gas phase oxidation with sulfur trioxide gas and plasma treatment (13–15), etc.

Plasma treatment has proved to be an effective method for surface modification of materials (16, 17). Plasma generated by rf glow discharge at room temperature, as used in this study, contains free radicals, positive and negative ions, electrons, metastable molecules and UV radicals that have enough energy to break chemical bonds such as C-C, C-O and C-H in substrate materials. These excited particles bombard the surface of the substrate materials, resulting in microetching necessary for mechanical interlocking and forming functional groups necessary for chemical bonding. Through plasma treatment, the surface energy can be increased. Besides, it is a dry process and therefore has advantages over an acid etching process in the reduced energy consumption and environmental contamination without producing waste solution. It has been widely used in the microelectronics industry. Wightman et al. have completed a great deal of successful work in applying plasma treatment to improve the adhesion between carbon fibers and polymer matrices (18–21). There also are reports about applying plasma treatment in improving adhesion of 3-dimensional carbon fiber reinforced plastics with electroplated metal films (22, 23). However, there are no known reports about applying plasma treatment in improving adhesion of carbon fibers with their wet-deposited metal films.

In this study, plasma surface treatment was first applied in the electroless deposition of copper film on carbon fibers. Air and nitrogen glow discharge were used to replace chromic acid in the $CuSO_4$-HCHO electroless system and to improve the adhesion between carbon fibers and the copper films. An orthogonal table $L_9(3^4)$ was used to study the effects of discharge pressure, gas, power and time on copper layer uptake. SEM, RAIR and XPS at different depth were applied to characterize the physical and chemical changes of the surface of the carbon fibers. A mechanism of plasma treatment effects on copper electroless deposition on carbon fiber surface is also suggested.

Experimental

Materials

PAN-based carbon fibers and carbon films were used in this study. The carbon fiber was obtained from Donghua University and we prepared the carbon film. The PAN film was obtained by a solution casting method. Then, the film was oxidized and carbonized. The carbonization temperature was 1500°C for the fiber and the film. Carbon film was used for obtaining XPS spectra at different depth more accurately than on fibers. Other chemicals were all of chemical grade and were used as received.

Copper Deposition Experiment

Electroless deposition of copper film on carbon fibers and carbon films was carried out through the $CuSO_4$-HCHO oxidation and reduction system according to a common formula for metalization of plastics (24). The main reaction steps and the chemicals used are summarized in Table 1.

Plasma treatment was used to replace chromic acid or sulfuric acid pretreatment in this study. After each step, the samples had to be washed with distilled water to avoid bringing the previous solution to the following one and to avoid causing the deposition to occur in the solution, rather than on the surface of the fibers. After completing the deposition, the samples were washed with distilled water 3 times and then dried in a vacuum oven at 80°C for 3 h. After that, the copper uptake on the fiber surface was found by determining the initial and the final weight of the fiber before and after the deposition.

Plasma Treatment

A plasma system based on a radio frequency (13.56 MHz) generator was used in this study. The custom-built reactor has been described previously (25). The samples were placed in the middle of the reaction chamber. The gases for the plasma treatment were nitrogen and air. When using nitrogen, the chamber was evacuated to a pressure of 0.6 Pa before nitrogen was introduced. Copper deposition (as in the Copper Deposition Experiment section) was done immediately after the samples were taken out of the chamber.

Surface Characterization

Surface Topography. The surface topography was observed with a Cam-Scan-4 scanning electron microscope (SEM). The surface and cross section changes were examined and compared. The fibers were dipped into liquid nitrogen which temperature is 77 K, and taken out and broken with tweezers. Thus, the cross section of fiber was made.

Table 1
Deposition reaction steps, chemicals and main reactions

Step	Formula	Reactions
Pretreatment	Chromic acid or sulfuric acid	Replaced by plasma treatment in this study
Sensitizing	$SnCL_2 \cdot H_2O$, HCl, Sn	$Sn + Sn^{4+} \longrightarrow Sn^{2+}$
Activating	$AgNO_3$, NH_4OH	$2Ag^+ + Sn^{2+} \longrightarrow Sn^{4+} + 2Ag \downarrow$
Deposition	$CuSO_4$, $KNaC_4H_4O_64H_2O$, NaOH, Na_2CO_3, HCHO	$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 \downarrow + NaSO_4$ $Cu(OH)_2 + 3C_4H_4O_6^{2-} \longrightarrow Cu(C_4H_4O_6^{2-})_3]^{4-} + 2OH^-$ $2Cu(C_4H_4O_6^{2-})_3]^{4-} + HCHO + 4OH^- \xrightarrow{Ag} 2Cu + 6C_4H_4O_6^{2-} + CO_2 + 3H_2O$

Surface Chemical Composition. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemical composition changes after plasma treating. XPS spectra were collected with a Microlab M2 produced by General Electric Co. in a constant resolution mode (CAE). The constant pass energy was 20 eV. The Al Kα X-ray source was operated at 3 kV and the discharge current was set to 20 μA. The voltage of photoelectron tube and the base pressure were 2.6 kV and 2×10^{-12} Pa, respectively.

Argon etching is widely employed in XPS to determine chemical composition with depth. Because carbon fibers are very fine (several micron), it is difficult to get a uniformly etched depth. So carbon films with the same carbonization temperature as that of carbon fibers were used in this study. Through controlling the etching time of argon (voltage-5 kV), the composition distribution at different depths of the film was obtained. A roughly estimated first depth under the outmost surface was 60 Å and the second depth was 100 Å according to the steel etching rate of 2 Å/min at the same etching conditions. Because carbon fibers can be etched more easily than steel at the same conditions, the actual depths were greater than the estimated ones.

Core level spectra of C_{1s}, O_{1s} and N_{1s} were obtained by narrow scans. The data deconvolution of the spectra, such as the smoothing, fitting and peak area calculation, was carried out with the in-house software.

Surface Chemical Structure. Infrared measurements were done with a Bio-Rad FTS-40 FTIR spectrometer at a resolution of 4 cm^{-1}. Reflection spectra were collected and compared for the untreated and plasma treated carbon fibers with a variable angular specular reflectance attachment that was set to an incidence angle of 60°.

Results and Discussion

Effects of Plasma Treatment on the Copper Uptake

An orthogonal $L_9(3^4)$ factor-level table was used to investigate the effects of plasma working conditions on the copper uptake of the carbon fiber surface. The investigated factors were discharge power, pressure, time, and gas kind. The selected levels according to experience are as given in Table 2.

Nine experiments were completed according to Table 2. The results are summarized in Table 3.

Table 2
$L_9(3^4)$ factor and level design for plasma treatment

	Factor			
Level	A (power(w))	B (time (min))	C (pressure (Pa))	D (gas)
1	20	10	13.3	N2
2	25	30	20.0	Air
3	30	50	40.0	Air

Table 3
Effects of plasma treatment on the uptake of copper layer

Experiment no.	Factor				
	Power	Time	Pressure	Gas	Uptake%
1	1(20)	1(10)	1(13.3)	1(N2)	40.11
2	1	2(30)	2(20.0)	2(Air)	28.43
3	1	350	3(40.0)	2(Air)	44.00
4	2(25)	1	3	2	38.98
5	2	2	2	2	44.51
6	2	3	1	1	24.43
7	3(30)	1	2	2	28.05
8	3	2	3	1	28.23
9	3	3	1	2	30.36
Total (K1)	112.54	107.14	94.90	92.77	Sum = 307.10
Total (K2)	107.92	101.17	100.99	214.33	
Total (K3)	80.71	98.79	111.21		
Average (K1)	37.51	35.71	31.63	30.92	
Average (K2)	35.97	33.72	33.66	35.72	
Average (K3)	26.90	24.70	37.07		
Deviate(R)	10.61	11.02	5.44	4.80	
Better level	A1	B1	C3	D2	
Factor order	B > A > C > D				

Compared with the copper uptake of 18.65% for the untreated carbon fibers, the copper uptake increases significantly for the plasma treated fibers. Among the four factors considered, discharge power and discharge time have more influence on the copper uptake than pressure and gas kind. Within the level range considered, the power, pressure and time for the optimum uptake of the copper layer were 25 w, 40 Pa and 10 min. Air discharge was found to be more effective than nitrogen discharge.

SEM Observations

Figures 1 and 2 show the surface of untreated and air plasma-treated carbon fiber observed by SEM. As shown in Figure 1, the untreated carbon fiber surface appears smooth; only longitudinal, spinning process related striations are visible. After 10 min air plasma treatment, etching pits are clearly seen (Figure 2), resulting in high surface roughness and increased surface area. The SEM pictures of the copper deposited carbon fibers are shown in Figures 3 and 4. For untreated carbon fibers, large and separate copper grains are seen on the surface of a large number of carbon fiber, as shown in Figure 3. For plasma treated carbon fibers, a uniform copper layer is seen on their surfaces, as shown in Figure 4. The adhesion between carbon fibers and copper films was observed to be tighter for air plasma treated fibers than for untreated ones as shown in Figures 5 and 6.

Because plasma-treated carbon fibers have a rougher surface than the untreated ones, this rough surface may hold more sensitizing metal ions, activator ions and catalyst Ag grains on its surface, therefore creating more catalyst centers and increasing the copper

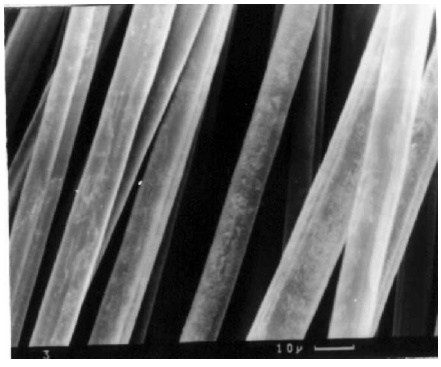

Figure 1. Surface of untreated carbon fiber.

uptake. In the copper deposition process, a rough surface holds more catalyst Ag grains than a smooth surface. Besides, copper ions can easily grow into smaller copper crystals centered on more catalyst Ag grains and develop into a uniform film as shown in Figure 4. The rough surface may also create mechanical interlocks between the carbon fibers and the metal copper, therefore increasing their adhesion as seen in Figures 5 and 6. Inversely, large and separate copper grains are easily formed if there are not enough Ag catalyst centers on the smooth surface. Therefore, from the above SEM observations, a mechanism for plasma-treated carbon fibers is suggested in which plasma-created surface roughness plays a critical role in the greater copper uptake and a uniform copper film. This physical roughness also enhances the adhesion between carbon fibers and the copper films.

XPS Analysis of Plasma Treated Carbon Film

Figure 7 shows the C_{1s}, O_{1s} and N_{1s} core level spectra at 60 Å beneath the outermost surface of the plasma treated carbon fibers compared with the untreated ones (assignments listed in Table 4). The untreated and plasma-treated carbon film surface contain considerable oxygen but no detectable nitrogen, although the carbon film carbonized over 1500°C should have contained only a little oxygen and nitrogen.

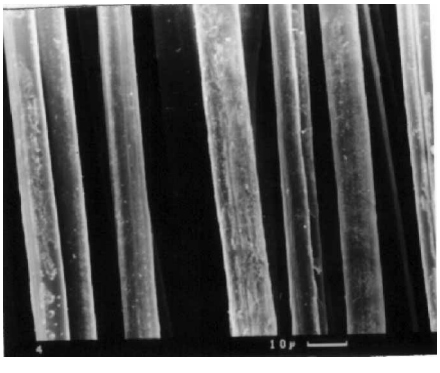

Figure 2. Surface of air plasma treated carbon fiber.

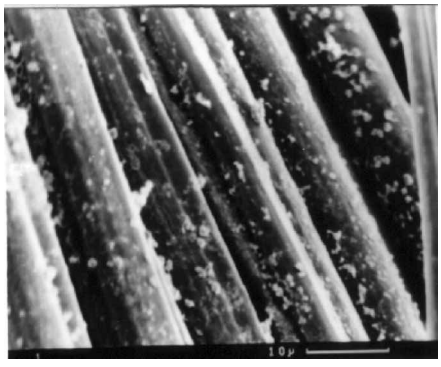

Figure 3. Copper coated carbon fiber surface (without plasma treatment).

For the untreated carbon film, the oxygen comes from the high absorbency of the carbon film for oxygen (12). For the air plasma-treated carbon film, plasma treatment adds more oxygen on the carbon fiber surface in addition to the absorbed surface oxygen. This is because in the plasma treatment process, the air plasma bombards the carbon film surface and introduces oxygen groups and other highly reactive radicals. These reactive radicals could react with oxygen and moisture in the atmosphere on exposure to air and form surface oxygen groups. This explains the higher oxygen content in air plasma-treated carbon film than in the untreated one at the same depth. That no nitrogen was found for air plasma-treated carbon film may be caused by the lower reactivity of nitrogen in the plasma. Other researchers have shown that nitrogen plasma also introduced much more oxygen than nitrogen on the carbon fiber surface (26). So, almost no nitrogen was detected in air plasma-treated samples.

The different carbon components of the core level spectra, assigned according to published references and relative concentration of each carbon functionality containing oxygen and the total oxygen content at each depth (27–31) and are summarized in Table 4. From this table, it can be seen that: 1) The surface layer of air plasma-treated carbon film contains a higher oxygen content than untreated ones; 2) The oxygen content decreases with depth slower for air plasma-treated sample than for untreated ones. This means that oxygen has penetrated to a greater depth in the air plasma-treated carbon films.

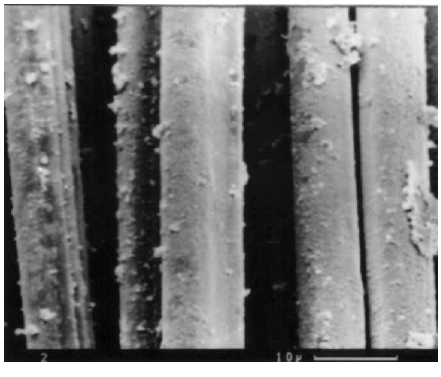

Figure 4. Copper coated carbon fiber surface (with plasma treatment).

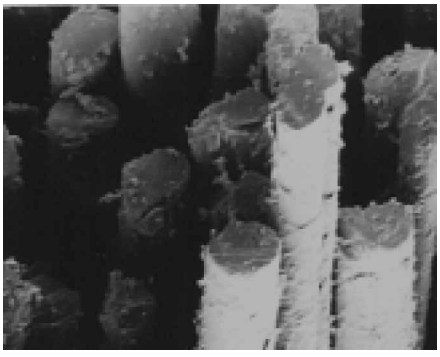

Figure 5. Copper coated carbon fiber cross section.

In the copper deposition process, sensitizing, activating and deposition are all chemical reactions taking place on the carbon fiber surface. Sn reduces Sn^{4+} in the solution into Sn^{2+}. Sn^{2+} clinging on the fiber surface reduces Ag^{+} into metal Ag grains. These Ag grains should stick on the carbon fiber surface first, after which they can serve as the catalyzing centers for the subsequent copper deposition. A highly wettable and rough surface is greatly beneficial to the permeation of the reactive agent and more Ag grains forming on the fiber surface. So, many kinds of pretreatment such as chromic acid and sulfuric acid are usually applied before these steps to increase the deposition uptake and to improve the adhesion between the copper film and the carbon fiber surface.

According to some researchers (32), the chromic acid pretreatment also introduces OH, C═O and COOH, etc. groups in the surface and that is exactly one reason for adhesion improvement in that case. As shown above, plasma treatment has the similar effects of incorporating oxygen groups on the carbon fiber surface. The results of Liston et al. showed that C-O-metal bonds exit in the plasma-treated carbon fiber and metal film (33). So it is reasonable to believe, from the above XPS analysis, that the addition of oxygen polar groups into the greater depth of the carbon fiber surface is another reason for the increasing of copper uptake of plasma-treated carbon fibers.

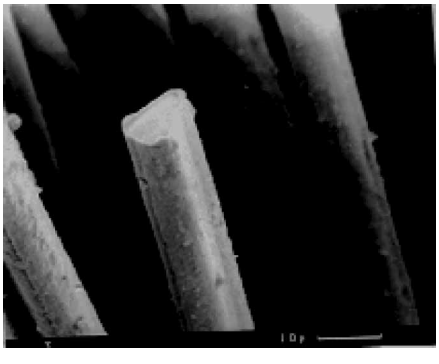

Figure 6. Copper coated carbon fiber cross section (without plasma treatment).

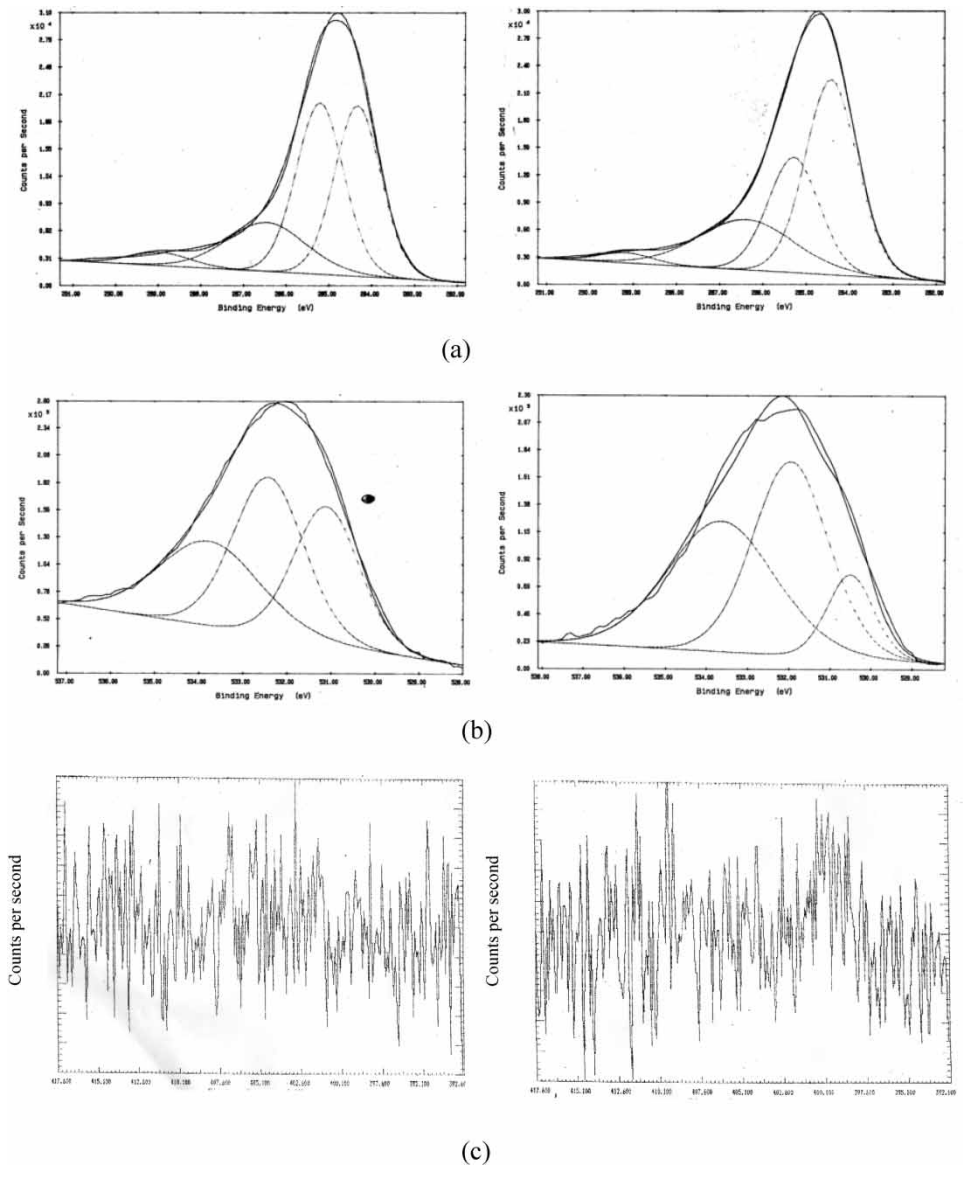

Figure 7. XPS spectra of untreated (left) and air plasma treated (right) carbon film.

In discussing the effects of types of gas on the copper uptake in the last section, it was noticed that the copper uptake of nitrogen plasma treated carbon fibers is lower than that of the air plasma-treated carbon fibers. This may also be caused by the lower content of the oxygen polar groups introduced by the N_2 plasma (26).

IR Investigations

In order to verify the oxygen functional groups existing in the plasma treated samples in comparison with the results of XPS, FTIR was applied. A typical FTIR spectrum of the air

Table 4
XPS data of air plasma treated carbon film

Sample	Depth (Å)	C1s				O1s			O1s/C1s	O Content (%)
		284 eV	285 eV	286 eV	288 eV	531 eV	532 eV	533 eV		
Untreated	0	0.35	0.53	0.12	0.00	0.47	0.23	0.30	0.26	0.21
	60	0.32	0.41	0.22	0.05	0.31	0.39	0.30	0.29	0.22
	100	0.38	0.39	0.19	0.04	0.39	0.35	0.26	0.07	0.07
Treated	0	0.59	0.29	0.09	0.03	0.13	0.60	0.27	1.04	0.51
	60	0.47	0.28	0.23	0.03	0.12	0.45	0.43	0.62	0.38
	100	0.42	0.39	0.15	0.04	0.18	0.64	0.18	0.17	0.14
Probable identification		C-C	C-O-C	Ph═O	COO	C═O	C-OH, C-O-C	COO		

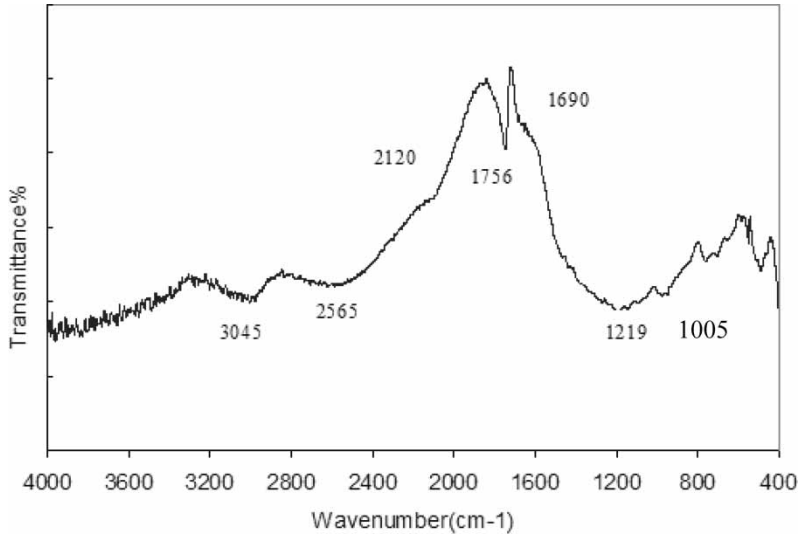

Figure 8. IR of carbon fiber surface after air plasma treatment.

plasma-treated carbon fibers is shown in Figure 8. This spectrum is the result after subtracting the untreated carbon fiber background spectrum. The vibration frequencies and their assignments for the air plasma-treated carbon fiber are shown in Table 5.

The spectrum in Figure 8 clearly indicates that several kinds of oxygen groups are incorporated into the surface of air plasma-treated carbon fibers. The band at 3045 cm^{-1} is due to OH stretch vibrations caused by hydrogen bonded carboxylic acid groups. The peak at 1219 cm^{-1}, caused by C-O stretching mode, corresponds with this assignment. The sharp peak at 1750 cm^{-1} is assigned as the C=O carbonyl stretching vibration. This carbonyl group may be related to aliphatic ketones, esters and aldehydes or carboxylic acid. The shoulder peak at 1690 cm^{-1} may result from the carbonyl stretching vibration related to quinone groups as there are a lot of aromatic carbon rings in the carbon fibers. The broad peaks at 1219 cm^{-1} and 1005 cm^{-1} correspond to the combination of several vibration modes such as=C-O stretching in alkyl aryl ethers and aryl aldehydes in aromatic rings.

From the above IR analysis, we confirm that the oxygen groups exist in air plasma-treated carbon fiber surface mainly in the form of carboxylic acid COOH, aromatic

Table 5
The IR vibration frequencies and their assignments for air plasma treated carbon fibers

Frequencies (cm^{-1})	Assignment
3045	OH str. In carboxylic acid
1750	C=O str. In carboxylic acid, aliphatic esters, ketons or aldehydes
1690	C=O str. In aromatic carbon rings
1005, 1219	C-O str. In aryl esters or aldehyde

ketones Ph═O, aldehydes or esters C-O or COO^-, in agreement with the results of XPS. It is because of these polar oxygen groups introduced into the plasma treated carbon fiber surface that leads to the wetability improvement of the carbon fiber surface. Therefore, the sensitizing and activating solution can permeate a greater depth below the carbon fiber surface more easily. Combining with the roughing effects caused by the plasma treatment as observed in SEM, a greater copper uptake can be obtained for air plasma treated carbon fibers and the adhesion between the copper film and the carbon fiber is improved.

Conclusions

We first used plasma treatment to replace chromic acid pretreatment in a electroless deposition system. Experimental results show that this treatment method is effective for improving the copper uptake, obtaining a uniform copper film on carbon fiber surfaces and increasing their adhesion. Air plasma is found to be more effective than nitrogen plasma. At the working conditions considered, air plasma can increase the copper uptake by as much as 239%. Discharge power and time have more influence on the copper uptake than discharge pressure and the type of gas.

SEM, RAIR and XPS measurements and analysis show that plasma treatment gives a rough surface and incorporates more polar oxygen groups into a greater depth of carbon fiber surfaces. This rough surface is assumed to hold more catalysts and to form fine copper crystals. Therefore a uniform copper film is easily obtained and the copper uptake of plasma-treated carbon fibers is also greater than the untreated ones. Besides, polar oxygen group incorporation makes the carbon fiber surface more wettable, which is helpful to the permeation of the sensitizing and activating agents into a greater depth of carbon fiber surface. This also enhances the plasma treatment effects in increasing the copper uptake, improving the uniformity of the film and the adhesion between the copper film and the carbon fibers.

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