

A New Method of Doping Pyrolytic Graphite Utilizing Laser Heating in the Presence of Organic Heteroatomic Vapors

C. A. Kuper and M. M. Labes*

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

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When pyrolytic graphite is heated with a high-energy pulsed Nd:YAG laser in the presence of pyrrole or 3-methylthiophene vapors, the surface becomes doped with nitrogen or sulfur, respectively. The time frame of the intense heating is such that the lattice does not undergo any extensive rearrangement, and the methodology results in modification of the properties of the graphite by introducing donor or acceptor atoms into the array. The doped graphites are analyzed by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), X-ray diffraction (XRD), X-ray fluorescence microscopy (XFM), and/or scanning electron microscopy (SEM). XPS indicates chemical shifts in the carbon 1s energies for the nitrogen and sulfur doped samples. AES shows changes in the carbon KLL emission energies upon doping. Correlation of these shifts with the XRD allows definition of the chemical bonding present. Nitrogen is covalently bound to carbon at the domain edges and at trigonal sites, breaking the local aromaticity of the lattice. Sulfur, on the other hand, is interstitially located, resulting in a small lattice expansion along the *c*-axis of ~ 0.01 Å, and is easily removed by Ar ion sputtering.

Introduction

Doping of a graphite lattice by introducing donor or acceptor atoms is expected to modulate its electronic and physical properties. Examples of additives which have been shown to affect the properties of graphite are boron, nitrogen, and sulfur. Boron doping can be accomplished by diffusion of elemental boron (2500–3000 °C) or boric acid (1700 °C) into a pregraphitized carbon. The boron is known to enter the lattice substitutionally at trigonal sites.¹ Boron doping has been shown to increase the conductivity of the graphite and the degree of graphitization.^{2–4} Nitrogen incorporation is frequently accomplished by the thermal decomposition of appropriate precursor materials such as heteroaromatic hydrocarbons or polyacrylonitrile, the latter being a common starting material for the preparation of carbon fibers. Nitrogen has also been shown to increase the conductivity of graphite,⁵ although how and where it is situated in the graphite lattice is less well-understood than for boron. Preparative routes for sulfur incorporation into graphitic carbons are similar to those for boron. They involve diffusion of H₂S or elemental sulfur at reaction temperatures of 500–1000 °C.^{6,7} How sulfur interacts with the graphite lattice still remains in question. Nitrogen containing pyrolyzed carbons have a low

thermal stability. All of the nitrogen is driven out of the lattice by heat treatment at 1800 °C.⁸ Sulfur-containing carbons also show a low-temperature loss of sulfur upon heat treatment (800–1400 °C).⁶ Interpretation of these results combined with electrical measurements allows one to conclude that nitrogen and sulfur are not substituted at trigonal sites, but rather decorate domain edges or lie interstitially in these materials. The expulsion of nitrogen often initiates ordering of the graphite. An ordered graphite containing nitrogen is therefore impossible to prepare by the pyrolytic route.

In this laboratory, it was observed that nitrogen and sulfur doping of graphite rods could be achieved during an arc discharge in the presence of organic heteroaromatic vapors, a process which involves intense heating for short time periods. In seeking a method to accomplish such doping in a controlled manner, a technique was developed in which a pulsed 300 W Nd:YAG laser beam was incident on pyrolytic graphite (PG) samples while they were exposed to a vapor stream containing a source of nitrogen or a source of sulfur. Since the time frame of the irradiation could be restricted to short repetitive pulses, the processing could be controlled so that the fundamental graphite lattice would not be changed during the heating. In this manner, nitrogen-doped PG was prepared at white hot temperatures and the chemistry of the nitrogen substitution appears to be profoundly changed. Spectral evidence indicates nitrogen substitution into trigonal sites, similar to the results achieved in diffusing boron into the graphite lattice. Reports of boron substitution

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into graphite at trigonal sites have been based upon X-ray diffraction (XRD) measurements of crystallite size and *d*-spacing.^{4,9} Results in this work that support this finding with nitrogen include XRD measurements as well as X-ray photoelectron spectroscopy (XPS). Sulfur, on the other hand, is too large to occupy substitutional sites in a carbon lattice and possesses much less similarity to carbon in its bonding geometry and electron configuration. It is found that sulfur enters the graphite lattice as an interstitial dopant under these processing conditions.

Experimental Section

Sample Preparation. First, 1 cm × 1.5 cm × 2 mm pieces of PG, obtained from Advanced Ceramics, were placed in a stainless steel reaction chamber equipped with a Suprasil quartz window, gas inlet, gas outlet, and multiple sample beds. The sample beds were made of stainless steel and were insulated on the bottom with Marinite, a high-temperature insulating fiber. Vapors of 3-methylthiophene or pyrrole, at a concentration of 0.1% in an Ar stream, were passed through the reaction chamber. The samples were irradiated in this environment for a total of 30 min each, consisting of three 10 min periods of pulsed irradiation with a 20 s off time between each period. Sample processing was accomplished using a 300 W fixed optics Nd:YAG processing laser operating at 13 J applied energy, 4.5 Hz repetition rate, and 8 ms pulse length (power ~18 kW cm⁻²), under computer-modulated control. The irradiation was conducted under ambient pressure and constant gas flow. The samples were heated to a uniform white hot temperature (~3500 K). There was virtually no soot formed on the walls of the chamber as a consequence of the irradiation. A reference sample of PG was processed following the same conditions in the absence of the reactive gas. Some sulfur-doped samples were prepared in a single-sample Pyrex cell with a quartz window and gas inlet and outlet. This chamber was connected with Tygon tubing to a bubbler containing boiling 3-methylthiophene, obtained from Aldrich, through which Ar gas was passed. In this latter cell, some ablation of the graphite was seen during certain runs, but the majority yielded no soot.

Spectroscopic Characterization. Samples of sulfur-doped PG were prepared for scanning electron microscopy (SEM) by Soxhlet extraction in refluxing toluene. The toluene remained clear, implying little or no formation of soluble carbon compounds, such as the fullerenes, on the surface of the PG. After extraction, the samples were dried overnight in vacuo. Photomicrographs of the surface were taken to characterize the different regions of the surface: (a) the spot where the laser impinged directly on the sample, producing a shallow pit 3 mm in diameter; (b) the surrounding region where less doping occurred. SEM was performed using a Phillips 501 instrument operated at a 15 keV acceleration voltage.

X-ray fluorescence microscopy (XFM) was performed at Brookhaven National Labs on the X-ray microprobe, beam line X26 A, using synchrotron radiation. A 500 μm × 100 μm image of the surface was compiled as well as spectra on a 10 μm spot. The white beam was defined using a 10 μm pinhole and the images were obtained by scanning through the beam in 30 μm steps. The fluorescence spectra were collected at each point with a Si(Li) energy-dispersive X-ray detector. The XF spectra were taken in the pitted area of the surface as well as on the surrounding area to compare surface concentrations. The expected surface penetration of the beam is 100 μm into the sample.

Auger electron spectroscopy (AES) of the KLL transition associated with the C(1s) core hole energy was studied for samples of nitrogen-doped PG, sulfur-doped PG, and irradiated undoped PG (reference sample). The spectra were taken under

5×10^{-9} Torr with an emission current of 4.1 μA using a 3 keV beam voltage. Counts were averaged over a 500 μm × 200 μm area of the surface.

XPS was carried out in a EA10/1000 Leybold Heraeus spectrometer, at 10⁻⁹ Torr, using MgKα radiation (energy 1253.6 eV) at 140 W total power, with a 40 eV pass energy to a hemispherical mirror analyzer. A correction for the work function of the analyzer was made by referencing the Au(4f) lines, and is automatically taken into account during data acquisition. Counts were averaged over a 500 μm × 500 μm area of the sample. Spectra of the C(1s), O(1s), N(1s), or S(2p) core levels were acquired for nitrogen-doped PG, sulfur-doped PG, and reference PG, both before and after bombarding the surface with Ar ions for 10 min, at an Ar pressure of 5×10^{-4} Torr using a 4 keV beam voltage. The C(1s) peaks were fit by a share ware computer program "XPS Peak Fit". The peak positions and full width at half-maximum (fwhm) were fixed (fwhm at 1.1) and only the peak heights were changed to best fit each spectrum. The C(1s) core level peak is decomposed to a four-peak fit using a 20% Lorentzian and 80% Gaussian function. The four peaks account for the binding energies (BEs) of sp²-hybridized carbons at a trigonal site, 284.5 eV, edge carbons, 284.3 eV, sp³-like carbons, 285.5 eV,¹⁰ and a carbon oxide, 286.6 eV. The high binding energy tail is due to final state effects which arise from the high conductivity of the graphite. These effects originate from metallic core hole screening, reflecting the excitation spectrum of the conduction electrons.¹¹ Bombarding the surface of the graphite with Ar ions resulted in a change of the peak morphology of the C(1s). The C(1s) peak was broadened and its intensity decreased consistently for all samples. Peak broadening of the C(1s) after ion bombardment has been attributed to the formation of amorphous carbon surface states.¹² Although sputtering the surface of the graphite gave valuable information on the relative penetration depth of dopant atoms, it remains difficult to separate the effects of sputtering from the changes in atomic concentrations of the dopant atoms. For this reason the C(1s) peaks of the sputtered samples are not shown, but the effects of sputtering are discussed.

X-ray diffraction (XRD) data were obtained on a Rigaku D/Max2 instrument, using CuKα radiation. The samples were attached to Kapton 3M no. 92 tape with a clay mount in the center of an aluminum disk. The samples were then pressed parallel to the plane of the disk. XRD measurements were made in a spinning cell goniometer.

Results and Discussion

Sulfur-Doped Pyrolytic Graphite. The laser treatment of PG in the presence of organic vapors containing sulfur resulted in doping levels of 0.5% atomic concentration (ac%). XF spectra on the sulfur-doped PG showed sulfur incorporation at levels of 0.5 ac% in the smooth surface area and 5 ac% in the pit formed by the laser beam. The XFM map of the smooth surface area shows that sulfur is distributed throughout the entire surface area but increases in concentration in certain localized regions. It is possible that these are areas of surface defects in the graphite crystal.

The image obtained by SEM shows that the pitted area formed by the 3 mm defocused beam spot on a sample of sulfur-doped PG consists mainly of small spherical carbon clusters. The indication that the sulfur concentration in the pitted area is 10 times greater than the smooth surface area is consistent with sulfur-doping

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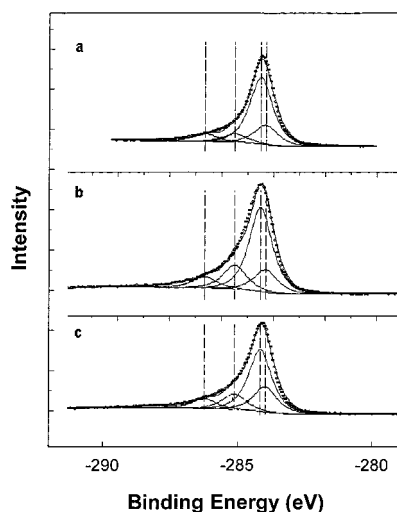


Figure 1. XPS of the C(1s) core level for (a) reference PG; (b) nitrogen-doped PG; (c) sulfur-doped PG. All spectra are for unsputtered samples.

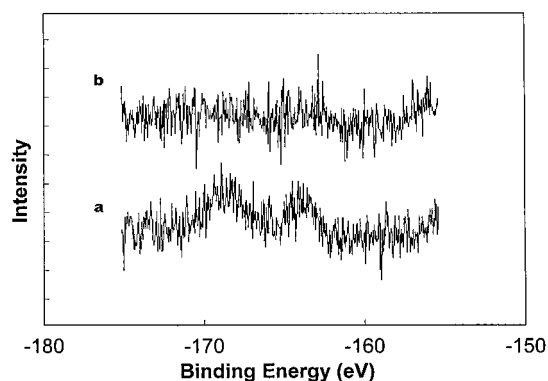


Figure 2. XPS of the S(2p) core level in sulfur-doped graphite (a) before and (b) after Ar ion bombardment of the surface.

levels of carbon soots prepared in these laboratories via arc vaporization. The doping levels in PG are consistently maintained at 0.5 ac%, on the smooth surface area.

AES confirmed sulfur-doping levels to be 0.5 ac%, by a computer program called "Auger Scan", available from RBD Enterprises. These spectra also reveal chemical shifts in the KLL transition associated with the C(1s) core hole energies of the doped samples. The sulfur-doped PG C(1s) peak appears at 272.9 eV kinetic energy (KE). The C(1s) peak of the irradiated undoped PG is evident at 272.1 eV KE. The oxygen content for both samples was 3 ac%. The sulfur-doped C(1s) is shifted 0.8 eV to higher KE.

XPS of the C(1s), S(2p), and O(1s) core levels were determined for the sulfur-doped graphite. The C(1s) spectrum is shown in Figure 1c and compared to the C(1s) spectrum for the reference sample in Figure 1a. The peak areas of the C(1s) of the sulfur-doped graphite decreases by $\sim 40\%$ relative to the reference sample. This decrease is associated with sulfur masking the signal of surface carbons. After bombardment of the surface with Ar ions, the S(2p) peak diminishes (Figure 2).

The decrease in the intensity of the C(1s) peak seen upon sulfur doping may be explained by a model in which the sulfur atoms are trapped in the graphite layers at defect sites and chemisorbed on the surface. In this case, the sulfur atoms would mask the signal of

Table 1. XRD Measurements for the Doped Samples and Pristine PG before Ion Bombardment

PG sample	2θ reflections		d_{002} (Å)	peak intensity (cps)		peak width (fwhm)	
	{002}	{112}		{002}	{112}	{002}	{112}
N-doped	26.1	85.0	3.409	39211	175.5	0.567	1.349
S-doped	26.0	85.1	3.428	42442	158.7	0.537	0.750
pristine	26.1	85.0	3.416	36330	159.1	0.568	0.808

the surface carbons and be easily removed by sputtering the surface. XFM shows that higher concentrations of sulfur exist in very localized regions throughout the surface. This result, combined with XPS data, and the ease with which the sulfur is removed by sputtering the surface, indicates that sulfur is located interstitially at surface defect sites, such as those that arise at the boundaries between domain edges, with a lesser amount in the bulk. The decrease in peak asymmetry of the unsputtered sulfur-doped PG as compared to that of the reference PG may be caused, in part, by electrons inhibited from falling below the Fermi level. In effect there is a widening of the band gap. These results agree with previous work in this laboratory on sulfur doping into DFP-2 grade graphite, where a decrease was observed in the conductivity of the graphite upon sulfur doping.¹³

The O(1s) peaks for the reference PG and sulfur-doped PG show identical behavior. Before sputtering there are two oxygens, a low BE O and a high BE O. After both samples are sputtered, there is an increase in the intensity of the low BE O and a decrease in the peak intensity of the high BE O. The changes in peak intensities of the C(1s) for sulfur-doped graphite are a product of only the sulfur interacting with the graphite, given that the amount of oxygen present is consistent for both samples.

XRD shows that the d -spacing of the pristine PG unit cell is 3.416 Å, and the d -spacing of the sulfur-doped sample is 3.428 Å. The XRD patterns for all samples show reflections from the {002}, {004}, and a weak reflection for the {112} planes of the graphite. The peak intensities [I(cps)], d -spacings ($c/2$), and fwhm values are given in Table 1. The intensity of the {112} reflection is also an indication of the crystallinity of the graphite. Changes in these parameters are small for the sulfur-doped graphite. There is a small reflection at 12 (22) present. This is not an identifiable reflection of graphite or any other form of carbon. It is believed to be an experimental artifact produced by an edge reflection of the sample in its mount. The fwhm of the {002} reflections for the pristine PG and sulfur-doped PG are 0.568 and 0.537, respectively. The intensities of these peaks are not changed significantly. The peak shapes in the XRD pattern for the doped sample has not been altered, but the lattice has expanded.

Nitrogen-Doped Pyrolytic Graphite. XPS of the nitrogen doped PG showed doping levels of 1.4 ac% by a ratio of the peak heights for the unsputtered sample, and 3.7 ac% after sputtering with Ar ions. Figure 3 shows the N(1s) spectra of the sputtered and unsputtered nitrogen-doped graphite. Figure 1b shows the C(1s) spectra for the nitrogen-doped PG before sputtering the surface with Ar ions. The C(1s) peak of the

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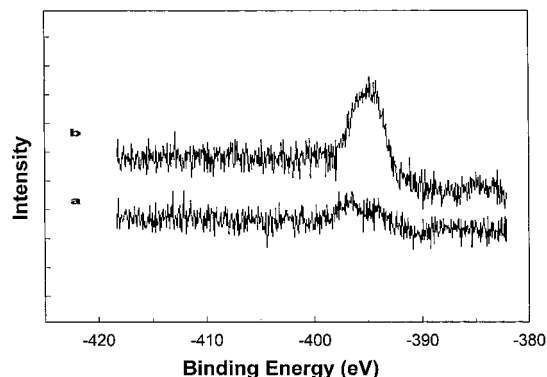


Figure 3. XPS of the N(1s) core level for nitrogen-doped graphite (a) before and (b) after Ar ion bombardment of the surface.

nitrogen-doped PG is at 284.4 eV BE, while the C(1s) for the reference sample is at 284.2 eV, a shift of 0.2 eV to higher BE. Upon deconvolution of the C(1s) peak for the reference PG and nitrogen-doped PG, it is seen that the intensity of the 284.3 eV peak is sharply decreased followed by a sharp rise in the intensity of the 285.5 eV peak relative to the reference sample. AES shows a peak shift in the carbon spectra of the nitrogen-doped sample of 0.4 eV to higher KE. Unfortunately, the nitrogen peak could not be observed in the Auger spectrum, although it is very intense in XPS.

XPS of the C(1s) core electrons in diamond shows a peak value of 285 eV for a completely sp^3 -hybridized carbon.¹⁰ The higher intensity of the 285.5 eV peak for nitrogen-doped PG indicates an increase in sp^3 -hybridization of the carbon, suggesting the possibility of aziridine radical formation at edge dislocations. A nitrogen attached in this manner breaks the aromaticity of the ring system and creates two sp^3 -hybridized carbons for every aziridine bond. The 284.3 eV peak is most likely associated with edge carbons. This peak is the second most intense in the reference sample and edge carbons would statistically be the second most abundant carbon in the graphitic network, the first most abundant being sp^2 -hybridized carbons lying in a plane surrounded on all sides by other carbons at 284.5 eV. Instead of a hydrogen forming the third bond with nitrogen in the aziridine complex, a carbon from a neighboring domain edge forms this third bond. After multiple rearrangement processes, this mechanism ultimately leads to increased graphitization around substitutional sites, as is the case in doping with boron.⁹ After the sample is sputtered for 10 min with Ar ions, the intensity of the N(1s) peak increases (Figure 3). This implies that most of the nitrogen is located below the first few monolayers. If this is the case, the Auger spectra, which is more surface-sensitive than XPS, would not reveal the presence of nitrogen.

The O(1s) spectra for the nitrogen sample, before and after sputtering, behave in the same manner as the reference sample and sulfur-doped PG. After sputtering, the intensity of the low BE oxygen increases, followed

by a decrease in the intensity of the high BE oxygen. The oxygen content in the nitrogen-doped graphite is consistent with the reference sample, so that one may conclude that spectral changes in the C(1s) of the nitrogen-doped graphite are due to nitrogen itself.

XRD gives a d -spacing for the nitrogen-doped sample of 3.408 Å, representing a contraction of the lattice by 0.008 Å. This contraction is due to the partial positive charge that forms on the carbons in the nitrogen-containing ring system. The positive charge causes contraction of the interlayer spacing by attraction of the delocalized electrons from the graphene layers. The 2θ reflections in the XRD pattern for the nitrogen-doped sample are given in Table 1. The increase in the intensity of the {112} reflection for the nitrogen-doped sample is indicative of an increase in the crystallinity of the graphite. The increase in the {112} reflection and the contraction of the unit cell is consistent with results for boron doping in pyrolyzed carbons, which show an increase in the degree of graphitization.¹⁴

Conclusions

Samples of nitrogen-doped graphite and sulfur-doped graphite have been prepared using a new synthetic approach involving a high-energy pulsed Nd:YAG laser. This method of doping does not distort the fundamental lattice configuration of the graphite. In this manner one is able to prepare samples of doped carbons that can be used to study fundamental issues regarding carbon atom interactions with heteroatoms at high temperatures. The binding dynamics of nitrogen with carbon are such that the nitrogen covalently binds to carbon at domain edges, leading to substitution after multiple rearrangements, breaking the aromaticity of this system. This results in an extension of the domain size and a contraction of the unit cell.

The behavior of sulfur with the graphitic network is markedly different from that of nitrogen. Sulfur does not form any covalent bonds with carbon. The sulfur atoms are located between the layers of the graphite and at defect sites in the crystal and are easily removed by sputtering the sample, indicating that the majority of the sulfur is close to the surface. XRD shows an expansion of the unit cell by 0.012 D.

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