

# Graphitization behavior of the boron-containing carbon film derived from polyimide

by

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The graphitization behavior of the boron-containing carbon film derived from polyimide was investigated. Boron doping was achieved by incorporation of an organo-boron compound, boric acid tri-methyl ester, into a PMDA/ODA polyamic acid precursor, followed by heat-treating the resultant polyimide film at a temperature range of 1000°C-2500°C to get boron-doped carbon film. The incorporation of boron to polyimide has a significant effect on the graphitizable nature of the polyimide film. A small concentration of boron less than  $1.0 \times 10^{-2}$  in the resultant carbon film was found considerably enhancing the graphitization of the carbon. This result would be helpful to an innovation using polyimide film in the fabrication of high quality graphite at lower heat treatment temperatures.

**Keywords:** Graphitization, Transmission electron microscopy, polyimide.

## 1. Introduction

In recent years, aromatic polyimide (PI) resins have found a place in the preparation of carbon materials due to their potential in the fabrication of C-C composites [1,2], graphitic carbons with high crystallinity [3, 4] and carbon molecular sieve films [5], and in other applications [6,7]. The graphitizable nature of PI-derived carbon film inspires us to study a possible fabrication of high quality graphite by piling up boron-doped PI films by hot-pressing at a low temperature. This method would be of great importance, since the fabrication process of high quality graphite usually necessitates pressurization at high temperatures from 3000 °C to 3600°C with much high cost [8]. Accompanying this investigation is the need to study the graphitizability of PI-derived carbon film, and the effect of boron doping on its graphitization behavior.

Doping of boron to PI, by incorporation of an organo-boron compound into a precursor polyamic acid solution, constitutes a simple route to reach a uniform distribution of boron in the resulting carbon (graphitic) structure and to avoid an additional high temperature exposure for introducing boron [9,10], and provides a

way to improve the intrinsic stability of carbon during oxidation.

This paper reports the experimental results for the graphitization behavior of the carbon doped with boron by this method.

## 2. Experimental

### 2.1 Preparation of polyimide-derived carbon films

The polyamic acid (PAA) solution was obtained as a solution of N, N-dimethylacetamide (DMAc) in 10 wt% concentration by stirring for 3 h in a flow of nitrogen gas, by reacting pyromellitic dianhydride (PMDA), with equimolar amounts of the 4,4'-oxydianiline (ODA). The PAA solution was then mixed with boric acid trimethyl ester for additional hour at the same condition to obtain boron-containing PAA. Both the boron-free and boron-containing PAA solutions were cast onto a glass substrate, elongated uniaxially, and placed in a drying oven at 60°C for 1 h to produce tacky PAA films that were then thermally imidized. The thermal curing was carried out in a vacuum oven with a temperature program that involves 2 h at 60°C, 0.25 h at 120°C, 180°C, 240°C and 300°C, respectively, and then 3 h at 350°C.

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The PI films in thickness around 25  $\mu\text{m}$  were cut into pieces of 30mm x 30mm. They were sandwiched between polished graphite plates and then heated to 1000°C at a heating rate of 2°C/min where they were carbonized for 1h in N<sub>2</sub>. The carbonized films were further treated at 1500-2500°C for 1h in Ar with a heating rate of 20 °C/min.

## 2.2 Characterization

Specimens of the films were submitted for elemental analyses of carbon, nitrogen, hydrogen, etc., while some of them were submitted for analysis of boron to determine the boron concentration. Table 1 shows the boron concentrations for the samples heat-treated in the temperature range of 1000°C-2500°C.

**Table 1** Boron content of PI-derived carbon films heat-treated at different temperatures.

Sample	B doping (wt%)	B/C atom ratio, $\times 10^{-3}$			
		1000°C	1500°C	2000°C	2500°C
CFB3	0.3	1.54	3.62		
CFB6	0.6	3.89	7.09	3.09	
CFB10	1.0	7.58	12.3	3.48	1.85
CFB12	1.2	8.36	16.8	9.94	3.92

X-ray diffraction measurements were carried out for film and pulverized samples of the PI-derived carbon, respectively. For determination of  $d$  spacing, measurements were taken at a scan speed of 0.25°/min in three ranges of 22-30°, 51-59°, and 72-90°, respectively. The lattice constant,  $c_0$ , average crystallite thickness,  $L_c$ , and crystallite diameter,  $L_a$ , were determined from (002), (004), (006) and (110) profiles, according to the standard method by Japan Society for the Promotion of Science.

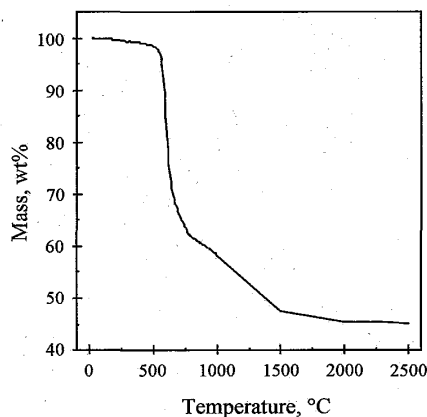
TEM observation was conducted for the PI-derived carbon films with a high-resolution transmission electron microscope (JEOL 2010) operated at 200 kV.

## 3. Results and discussion

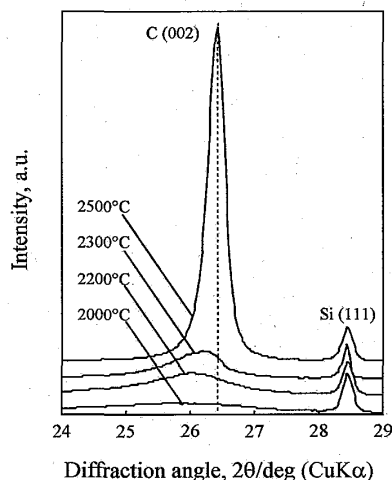
### 3.1 Structural change of boron-free film with heat treatment

Fig. 1 shows the weight changes in carbonization and heat treatment at high temperatures for the PI film. The heat treatment was performed in Ar. A rapid decrease of weight in a rather narrow temperature range from about 500°C to 700°C and a relatively gradual decrease

in the later wide temperature range from about 700°C to 2000°C were observed. The abrupt weight decrease is considered to be due to the formation of large amounts of CO and CO<sub>2</sub> evolved in the narrow temperature range around 500-700°C. The relatively gradual weight decrease seemed to be caused by the release of CH<sub>4</sub> and H<sub>2</sub> around 700-800°C and the evolution of N<sub>2</sub> and residual release of H<sub>2</sub> above about 800°C [11].



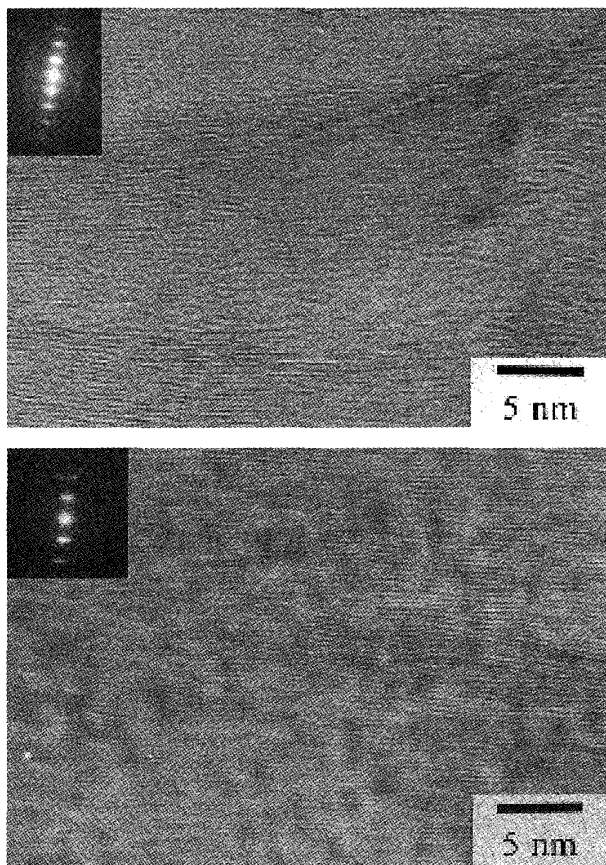
**Fig. 1** Weight change for PI film with heat treatment temperature during carbonization and graphitization.



**Fig. 2** (002) XRD patterns of the PI-derived carbon films heat-treated at different temperatures.

Fig. 2 shows the (002) XRD profiles of the pulverized samples of the carbon film heat-treated at the temperature range from 2000°C to 2500°C. The (002) peak shifted to a higher diffraction angle and the peak became sharper with the increase of HTT, suggesting a reduction in the apparent interlayer spacing  $d_{002}$  and an increase in the thickness of carbon layer stack  $L_c$  (002). It is noted that, the (002) peak for the sample heat treated at 2500°C was very sharp in comparison with the broad one for the 2300°C-treated sample; the

coalescence of crystallites into larger ones proceeded mainly above 2300°C and the graphitic structure in the carbon film heat-treated at 2500°C was much more developed.



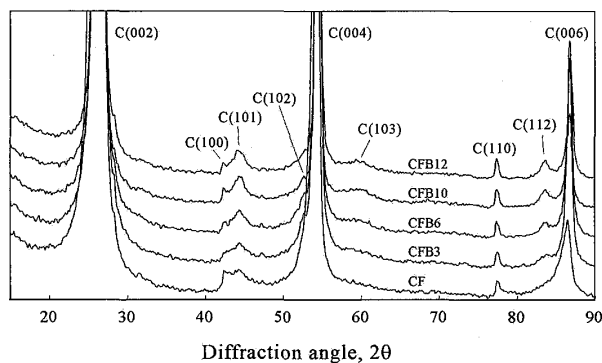
**Fig. 3** The lattice fringe images of the PI-derived carbon films heat-treated at 2300°C (upper) and 2500°C (lower). The inset patterns are their SAD patterns.

Graphitization, involving the joining of smaller segments of graphite layer plane together to form larger layer planes which are then translated into a proper stacking registry with neighboring layer planes, refers to a development of the three-dimensional graphite-like structure in the initially two-dimensionally ordered carbon [12]. A clear lamelliform texture in carbon film, observed from *n*-direction, could be illustrated by a BF image for the sample heat-treated at 2500°C, while only an obscure BF image, which illustrates a texture with lack of stacking order, could be obtained for the sample heat-treated at 2300°C. Fig. 3 shows the lattice images of the PI-derived carbon films heat-treated at 2300°C and 2500°C. The results of the TEM observations suggested the turbostratic structure for the carbon heat-treated at 2300°C and a three-dimensional graphite-like

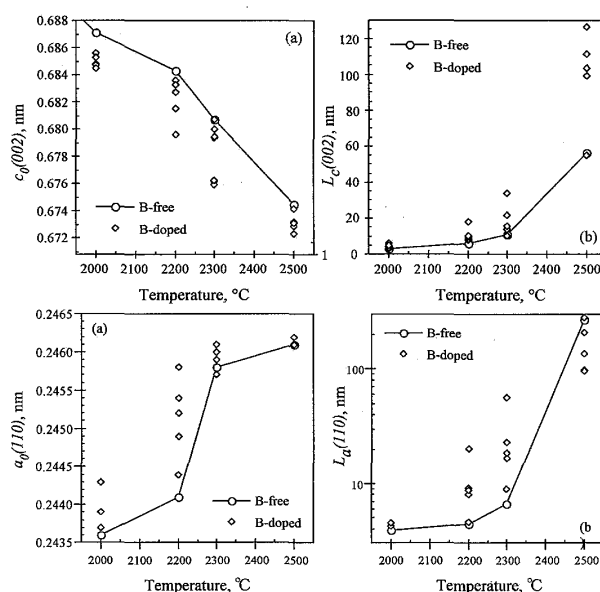
ordering in stacks of network layers for the carbon heat-treated at 2500°C.

### 3.2 Structural change with heat treatment for the boron-doping film

XRD measurement revealed that boron doping enhanced the graphitization of the PI-derived carbon film in the temperature range of heat treatment from 2000°C to 2500°C. Fig. 4 shows the XRD patterns for the pulverized samples of 2500°C-treated carbon films with different amounts of boron doping. There was a significant development of the modulation of (112) diffraction band that suggests a development of three-dimensional graphite structure as the amount of doped boron increased. A similar tendency was also found for other carbon peaks. Further, XRD patterns (002), (004), (006), (110), and (112) of carbon were analyzed in detail. As



**Fig. 4** XRD patterns of pulverized samples of PI-derived carbon films heat-treated at 2500°C with different levels of boron doping.



**Fig. 5**  $C(002)$ ,  $L_c(002)$ ,  $a(110)$  and  $L_a(110)$  of the PI-derived carbon films heat-treated at different temperatures.

boron was employed, overall the peaks shifted toward a higher diffraction angle indicating a lower value of  $d$  spacing. The boron doping catalyzed the graphitization of the carbon film.

Fig. 5 summarize the XRD results by crystallite parameters -  $c(002)$ ,  $L_c(002)$ ,  $a(110)$ , and  $L_a(110)$ . The results show that boron doping led to a reduction of lattice constant  $c$ , and an increase in  $L_c(002)$ ,  $a(110)$  and  $L_a(110)$  at almost all the heat treatment temperatures. The only except for the samples heat-treated at 2500°C with a decrease in  $L_a(110)$  due to boron doping is noted. However, the differences are not viewed as significant since  $L_a(110)$  exceeded 100 nm in this case.

It is shown that the structure of the carbon films heat-treated at 2000°C still remained in a turbostratic state, although boron doping led to a reduction in lattice constant  $c$  and an increase in  $L_c(002)$ ,  $a(110)$  and  $L_a(110)$ . On the other hand, the doped boron catalyzed the graphitization to a significant extent for the carbon films heat-treated in the range of 2200-2500°C. An obvious effect was found for the samples heat-treated at 2000°C and 2300°C by the parameters; boron doping promoted the conversion from the turbostratic structure to a graphitic structure - an ordering in stacks of network layers and a coalescence of crystallite to larger ones in the carbon film. It is considered that, doped boron contributes to the development of the ordering in stacks of network layers and the rearrangement of the neighboring crystallites that are already in relative preferred orientation within the carbon film, and thus improves the ordering in carbon layer stacks and enlarges the crystallite sizes in the carbon. For the samples heat-treated at 2500°C, the reduction in lattice constant  $c$  and the in-

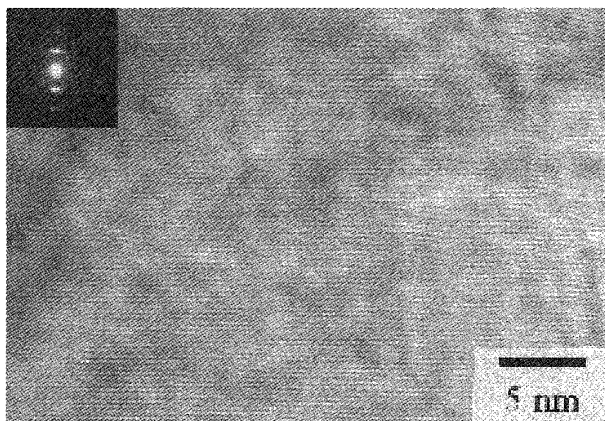


Fig. 6 Lattice fringe image of the PI-derived carbon film heat-treated at 2500°C with boron doping.

crease in  $L_c$  indicate that the three-dimensional graphite-like structure (referring also to the modulation of (112) peaks in Fig. 4) were much improved. The results of TEM observations conducted as shown in Fig. 6 provided further evidence for the structural characteristics. The SAD patterns and lattice fringe images in Fig. 6 show that ordering in stacks of carbon layer-plane was improved comparing with those shown in Fig. 3.

Graphitization is a thermally activated process involving the self-diffusion of carbon; structural defects in carbon are removed and strains are relaxed with the heat treatment in excess of 2200°C [13]. The lattice strain along the  $c$ -axis is much relaxed even for the specimens heat-treated at 2200-2300°C due to boron doping. Lowell [14] examined the solid solubility of boron in carbon over the temperature range of 1800°C to 2500°C, and found the substitutional solid solubility limit to be 2.35 atomic % at 2350°C. Turnbull et al. [15] found that the presence of boron as a substitutional species results in a contraction of  $c$ , whereas the presence of boron as an interstitial species restricts ordering of carbon layer planes. Substitutional boron atoms remain in their positions up to about 2000°C. At this temperature or higher, boron is removed by self-diffusion, leaving behind vacancies.

Diffusion of carbon via interstitial migration was argued the dominant diffusion mechanism during graphitization [16]. The activation energy ( $E_a$ ) for the self-diffusion of carbon in both the  $a$  and  $c$  directions is 6.8 eV, whereas the  $E_a$  for graphitization is established as about 10.5 eV [13]. Self-diffusion via interstitial migration is considered to dominate the first stage of graphitization that results in the increase of the layer-plane stacking dimension,  $L_c$ . The second stage of graphitization involves the lateral growth of crystallites that results in the increase of the crystallite diameter,  $L_a$ . The  $E_a$  for the lateral growth of crystallites is 10 eV [13]. The diffusion constants for the migration of boron in the  $a$  direction and the  $c$  direction of carbon were found to be 6320 cm<sup>2</sup>s<sup>-1</sup> and 7.1 cm<sup>2</sup>s<sup>-1</sup>, respectively. The diffusion constants for the migration of carbon in the  $a$  direction and the  $c$  direction were examined to be 82.8 cm<sup>2</sup>s<sup>-1</sup> and 1.81 cm<sup>2</sup>s<sup>-1</sup>, individually, being considerably lower than those for boron in carbon. Thus, boron may enhance the graphitization rate of carbon by an amount comparable to the increased

diffusivity of boron over carbon in the graphitic lattice, and an improvement of the self-diffusion of carbon via the vacancies left behind by the self-diffusion of boron.

Boron concentration for the samples decreased from 2000°C to 2500°C. The decrease may correspond to the self-diffusion of substitutional boron. For this reason, a small concentration of boron less than  $1.0 \times 10^{-2}$  in the resultant carbon film, in the present study, especially for the samples heat-treated at 2300°C and 2500°C, the substitutional boron atoms considerably contribute to the development of the graphitic structure and the reduction of the lattice.

#### 4. Summary

Doping of boron into carbon was achieved by incorporation of boric acid tri-methyl ester into a precursor PMDA/ODA polyamic acid, followed by heat-treating its resultant polyimide film at a temperature range of 1000°C-2500°C. This method of boron doping is considered to constitute a simple way with low cost to dope boron into carbon (graphitic) structure with uniform distribution of boron, avoiding additional high temperature exposure comparing with other methods conventionally employed.

Incorporation of boron to polyimide had a significant effect on the graphitizable nature of the polyimide film. A small concentration of boron less than  $1.0 \times 10^{-2}$  in the resultant carbon film was found considerably contributing to enhance the graphitization of the carbon. This result would be helpful to an innovation using polyimide film in the fabrication of high quality graphite at lower heat treatment temperatures.

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