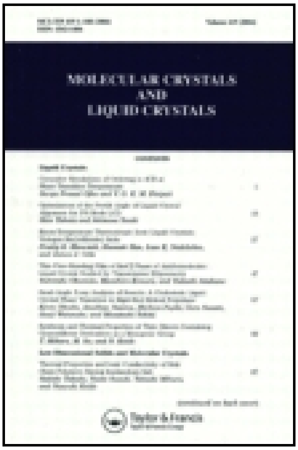

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# Novel Host Material For Graphite Intercalation Compound—High Quality Graphite Film Prepared from Newly Developed Polyimide Film

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# NOVEL HOST MATERIAL FOR GRAPHITE INTERCALATION COMPOUND—HIGH QUALITY GRAPHITE FILM PREPARED FROM NEWLY DEVELOPED POLYIMIDE FILM

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ABSTRACT Highly crystallized graphite film as a novel host material for graphite intercalation compound was prepared from a high-modulus-polyimide-film by carbonizing and then graphitizing it at high temperatures. Characterization of the graphite films obtained was made by measurements of interlayer spacing $d_{002}$, mosaic spread, residual resistivity ratio and Shubnikov de-Haas oscillation in Hall resistivity, and electron channeling micrography in a scanning electron microscope. All results of characterization show the high crystallinity of the present graphite films. Intercalation of $FeCl_3$ into the graphite film was carried out in a chloroform solution at room temperature. Enhancement of electrical conductivity was observed.

## INTRODUCTION

Recently, a graphitizable carbon film was obtained from a high-modulus-polyimide-film via polyamic acid gel.[1] This polyimide film may satisfy three conditions resulting in highly graphitizable carbon films; (1) flatness of original organic molecules, (2) high degree of their orientation and, (3) simple release of non-carbon atoms during carbonization. There is a possibility to obtain high quality graphite film from this polyimide film.

## PREPARATION

The precursor of the present polyimide film, polyamic acid, was prepared from pyromellitic dianhydride (PMDA), p-phenylenediamine (PPD) and 3,3',4,4'-tetraaminobiphenyl (TAB). The molar ratio of PMDA/PPD/TAB was 100/92/4. The polyamic acid thus obtained was dissolved in n-methylpyrolidone (NMP) at a temperature below 20°C, casted to a film, elongated uniaxially, and then imidized by stepwise heat-treatments up to 400°C. The polyimide film prepared is denoted hereafter as PPT. Thickness, tensile modulus and tensile strength of PPT are 45 μm, 882 GPa, and 0.196 GPa, respectively.

The films with a size of 10 x 26 $mm^2$ were cut out from the polyimide film, and were carbonized up to 900°C in nitrogen atmosphere by sandwiching between two artificial graphite plates with polished surfaces. An infrared heating equipment was used. The heating rate and residence time at the top temperature were 2°C/min and 1 hr, respectively. The carbonized films were then heat-treated between two polished artificial graphite plates in a graphite resistance furnace at temperatures of 2900, 3000 and 3200°C in a flow of dry argon gas. The heating rate was about 20°C/min, and the residence time at the top temperature was 30 min for heat treatments at 2900 and 3000°C and 10 min for 3200°C-treatment.

## CHARACTERIZATION

Characterization of the heat-treated films was made by X-ray diffractometry, measurements of the residual resistivity ratio and Shubnikov de-Haas oscillation in Hall resistivity at 4.2 K in the fields up to 6.5 T, and electron channeling micrography in a scanning electron microscope (SEM).

The X-ray measurements made on the samples were those of interlayer spacing $d_{002}$ and mosaic spread using Cu $K\alpha$ radiation. The measurements were carried out on the film samples. The $d_{002}$ value was determined from the 006 diffraction profile. In the 2θ range from 82 to 89°, only 006 diffraction was observed for each specimen and no trace of 112 line around 83.6°, suggesting high degree of orientation of hexagonal layer planes parallel to the film surface. Graphite crystallites were well organized, because the diffraction lines were so sharp that the lines due to $K\alpha_1$ and $K\alpha_2$ radiations were clearly separated, as shown in Figure 1 for the 3200°C-treated sample. The values of the interlayer spacing $d_{002}$ of the samples heat-treated at 3000 and 3200°C are the common value of 0.3354 nm, exactly the same as that of natural graphite, but 0.3356 nm for the 2900°C-treated sample. The latter value is exactly the same as that

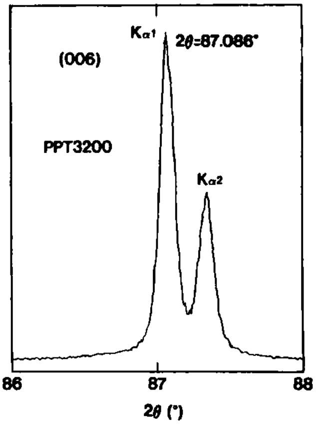

FIGURE 1 006 X-ray diffraction profile of 3200°C-treated sample.

obtained for pyrolytic carbon heat-treated at 3100°C for 15 min.[2]

Mosaic spread (MS) is defined by full width at the half maximum of the 002 diffraction intensity plotted against rotation angle of the film referred to the normal to the film surface at the diffraction angle giving the intensity maximum. The values of MS for the samples are listed in Table I. The 3000°C-treated specimen shows a little lower value than others, which may suggest a possibility to get much low mosaic spread at 3200°C by long holding.

TABLE I Mosaic spread (MS), RRR and average crystal size (L) of the samples.

| Sample | 2900°C-treated | 3000°C-treated | 3200°C-treated |
|---|---|---|---|
| MS (°) | 6.8 | 4.0 | 5.0 |
| RRR | 1.66 | 2.65 | 3.46 |
| L(μm) | 3 | 8 | 10 |

The residual resistivity ratio (RRR) is here defined by the ratio of the electrical resistivity at room temperature to that at liquid helium temperature. The values of RRR for the samples are also listed in Table I, the values being larger than unity. The RRR value of 3.46 for the 3200°C-treated sample corresponds to that of the regular quality HOPG specimen.[3]

Appearance of the Shubnikov de-Haas oscillation in the magnetoresistance and Hall effects gives an evidence of sufficiently large sizes of constituent crystals in the graphite sample. We used the Hall resistivity plotted against magnetic field up to 6.5 T at 4.2 K as a measure of the crystallinity of the specimens. The Shubnikov-de Haas oscillation in the Hall resistivity was observed well for the specimens, showing large crystal grain sizes in each sample. Figure 2 demonstrates the oscillation for the 3200°C-treated sample.

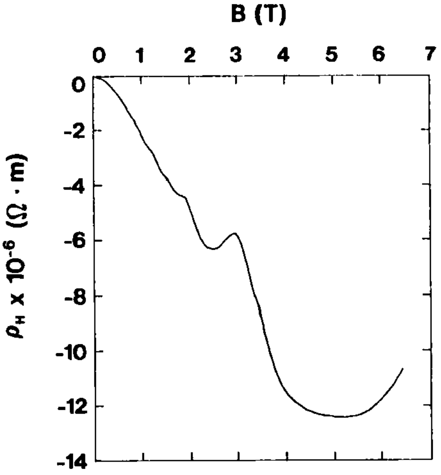

FIGURE 2 Hall resistivity $\rho_H$ at 4.2 K for 3200°C-treated sample plotted as a function of magnetic field B.

Size evaluation of crystals in the well oriented graphite sample can be made by the technique of the electron channeling micrography in the SEM.[4] When rocking an electron beam relative to a fixed point on the surface of the specimen, so that the angle of the beam changes with respect to the crystal lattice, the backscattered efficiency effectively varies discontinuously at the angle satisfied by the Bragg condition. The backscattered efficiency is enhanced for angles smaller than the Bragg angle $\theta_B$, and is lowered for angles larger than $\theta_B$. This effect is called the electron channeling effect. The electron channeling effect can be used in a micrograph mode of operation in the SEM. In this mode of operation the electron beam is always incident parallel to the optical axis of the microscope and the beam is scanned. The signals of the backscattered efficiency are imaged on the cathode ray tube as in the backscattered electron image mode. The crystallographic contrast effect occurs in a micrograph image, if the beam scans over a crystal boundary where the orientation changes abruptly and so also does the efficiency. The micrograph obtained by using such a contrast effect is called an electron channeling micrograph (ECM). Because of the polycrystalline nature of the present graphite films, the electron channeling contrast in the microscopic mode is effective in showing the growth of small crystals visually. At an acceleration voltage of 5 kV and with a tilt angle of 7.5°, ECMs produced by the contrast across the crystal boundary were obtained for the present graphite films. Figure 3 shows ECM for the 3200°C-treated sample. The brightest regions in

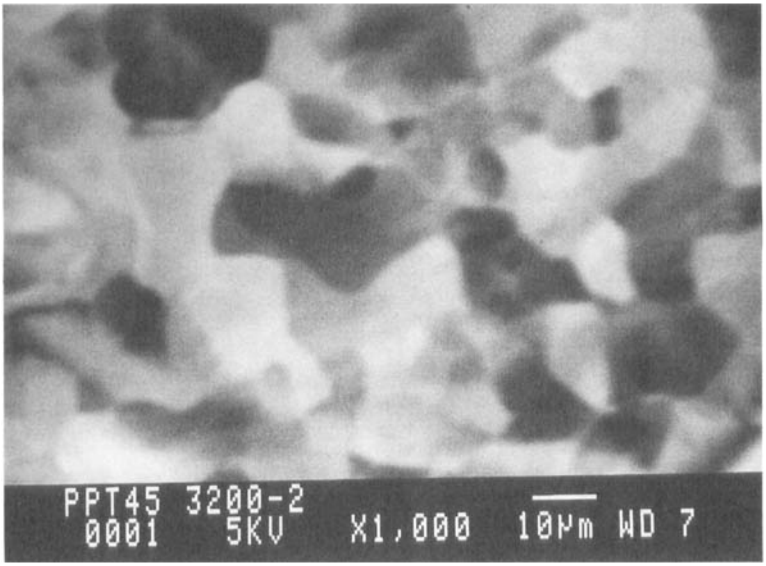

FIGURE 3 Electron channeling micrograph of 3200°C-treated sample.

the micrograph correspond to crystals whose [11.0] directions coincide with the direction of the horizontal axis of the micrograph, in which the brightness of each region changes as a function of rotation angle referred to the horizontal axis. The same micrograph for the sample can be obtained at every 60° rotation that corresponds to the 6-fold symmetry of the graphite crystal. From the micrograph the average crystal size L can be evaluated. The average crystal size for each sample determined from ECM is given in Table I.

## INTERCALATION

Into the 3000°C-treated films with the size of 3 mm x 5 mm and 26 μm thick, $FeCl_3$ was intercalated in the chloroform solution at room temperature, resulting in two types of ternary compounds with iron chloride and chloroform.[5] After 20 days reaction in the dark, an intercalation compound with stage 6-7 structure (Type I) was obtained in the form of film, without any cracks and flaws. By the reaction in light, a film of another intercalation compound with the same stage structure but with different period along the c axis (Type II) was formed. In the type I ternary compound the spacing between adjacent carbon layers containing the intercalate layer is 0.94 nm, while that in the type II 1.18 nm. The values of the electrical conductivity measured at liquid nitrogen and room temperatures of the type I and II ternary compounds are listed in Table II, comparing with the data on the pristine graphite film. Enhancements in electrical conductivity and also in metallic-like character of electron conduction were attained.

TABLE II Electrical conductivity measured at liquid nitrogen and room temperatures of specimens ($\sigma_{77\ K}$, $\sigma_{room\ temp}$) of pristine graphite film and type I and II ternary compounds.

| Sample film | $\sigma_{77\ K}$ [S/m] | $\sigma_{room\ temp}$ [S/m] |
|---|---|---|
| pristine graphite film | $1.92 \times 10^6$ | $1.65 \times 10^6$ |
| $FeCl_3$-$CHCl_3$-GIC (type I) | $8.66 \times 10^6$ | $5.16 \times 10^6$ |
| $FeCl_3$-$CHCl_3$-GIC (type II) | $15.4 \times 10^6$ | $7.26 \times 10^6$ |

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