



Title	Anisotropy of Electric Conductivity of Carbon and Graphite Films Derived from Kapton-type Polyimide
Author(s)	Konno, Hidetaka; Yoneda, Atsuo; Habazaki, Hiroki
Citation	炭素, 2002(204), 171-173 https://doi.org/10.7209/tanso.2002.171
Issue Date	2002-10-07
Doc URL	http://hdl.handle.net/2115/72923
Rights	著作権は炭素材料学会にある。利用は著作権の範囲内に限られる
Type	article
File Information	tanso204-171.pdf



[Instructions for use](#)



Anisotropy of Electric Conductivity of Carbon and Graphite Films Derived from Kapton-type Polyimide

Hidetaka Konno*, Atsuo Yoneda and Hiroki Habazaki

(Received June 24, 2002, Accepted July 31, 2002)

Carbon and graphite films were prepared from the laboratory-made Kapton-type polyimide film, and the electric conductivities parallel, σ_{\parallel} , and perpendicular, σ_{\perp} , to the surface were measured at room temperature. Anisotropy of electric conductivity was observed even for the 700°C treated film and the ratio, $\sigma_{\parallel}/\sigma_{\perp}$, increased with raising heat treatment temperature (HTT). The carbon films formed at HTT=1200-1600°C showed nearly the same conductivity, and $\sigma_{\parallel}/\sigma_{\perp}$ in this range was 450-550. The conductivities and $\sigma_{\parallel}/\sigma_{\perp}$ ratio increased with further raising HTT up to 2800°C. The structural changes of the films were also investigated by using XRD and TEM.

KEYWORDS : Anisotropy, Carbon film, Electric conductivity, Kapton-type polyimide, Transmission XRD

1. Introduction

Aromatic polyimides have been known as the attractive precursors for producing carbon and graphite films, and some types of polyimide films are industrially used as starting materials to produce highly oriented graphite blocks. Accordingly, a large number of papers have been published on this subject¹⁾. One of the reasons is that the graphitizable polyimide films have a specific molecular orientation parallel to the film surface. This suggests that anisotropic properties may appear at low heat treatment temperature (HTT). The electric conductivities parallel to the film surface were reported for different polyimide films carbonized at HTT=500-1100°C²⁾. It, however, is not reported at which HTT the anisotropy of electric conductivity for carbonized polyimide films starts to appear. The electric resistivities of carbonized and graphitized Kapton films at 77K and room temperature have been reported for HTT=1000-3000°C³⁾, but again the data are only of the film resistance. In the present work, Kapton-type polyimide film synthesized in the laboratory was carbonized and graphitized at HTT=700-2800°C, and the electric conductivities parallel and perpendicular to the film surface were measured. The structural changes were also examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

2. Experimental

Kapton-type polyimide films (30 μm thick) were synthesized by casting polyamic acid solution on a glass plate and by thermal imidization at 200°C under vacuum, in the usual way⁴⁾. The film was cut into about 1×1 cm², and carbonization was carried out for 1 h in flowing argon. Due to the furnaces used, heating rate was 400 K h⁻¹ for HTT=700-1200°C and 300 K h⁻¹ for HTT=1300-1600°C. Graphitization was carried out for 30 min with the films preliminarily carbonized at 1000°C for 1 h : HTT was set in a range of 2000-2800°C⁵⁾.

The electric conductivity parallel to the film surface, σ_{\parallel} , was measured by van der Pauw's method⁶⁾ and that perpendicular to the surface, σ_{\perp} , by a DC two-probe method at room temperature. For van der Pauw's method, a fine copper wire was pasted at each corner of the film with silver paste. For the two-probe method, gold was sputter-deposited on each surface of the film in a square shape of about 6×6 mm², and a fine copper wire was pasted on each gold film. The film thickness was measured by a digital gauge (resolution : 1 μm). Reliability of the methods was examined by measuring the values of an HOPG film cleaved from a block for monochromator (Advanced Ceramics, Grade ZYA).

Measurements and analysis of XRD patterns were carried out in conformity with the specification standardized by JSPS (Japan Society for Promotion of Science)⁷⁾. The Cu Kα radiation and a specially designed sample holder were used, and diffraction patterns were measured both by the reflection and the transmission mode. The average interlayer spacing, d_{002} , and the lattice constants, a_0 and c_0 , were determined after correcting the diffraction profiles for Lorentz-polarization, atomic scattering and absorption factors, referring to the outer standard of thin HOPG specimen.

Carbon films formed at 1600°C were observed by TEM at an acceleration voltage of 200 kV, and selected area electron diffraction (SAED) was also carried out.

3. Results and Discussion

The value of σ_{\perp} measured for the HOPG film was 830 S m⁻¹ which was slightly larger than 400-660 S m⁻¹ reported for similar grade HOPG⁸⁾. The difference was probably caused by the thickness measurements, as the resolution of the gauge was not very high. It, however, is in a permissible range, so that the measuring method is acceptable.

The average electric conductivities, σ_{\parallel} and σ_{\perp} , of carbonized and graphitized polyimide films are plotted against HTT in Fig.1.

❖ Corresponding Author, E-mail: ko@eng.hokudai.ac.jp
Graduate School of Engineering, Hokkaido University : Sapporo, 060-8628, Japan

The values of $\sigma_{//}$ up to 1100°C are nearly the same with those of the laboratory-made Kapton-type polyimide film reported by Inagaki *et al.*²⁾. Accordingly, van der Pauw's method is useful to the present specimens. To examine the effect of the ambient humidity on the electric conductivity, $\sigma_{//}$ of the 1000°C treated film was measured under the saturated humidity at 60°C. The $\sigma_{//}$ changed only within the experimental error of the present method. This may be a logical outcome, because the electric conductivity of pure water is about $5 \times 10^{-6} \text{ S m}^{-1}$ at room temperature. Although the values of σ_{\perp} scattered slightly, the anisotropy clearly appeared at HTT as low as 700°C. The difference between $\sigma_{//}$ and σ_{\perp} increased up to about HTT = 1200°C, but both $\sigma_{//}$ and σ_{\perp} became nearly constant at HTT = 1200–1600°C, $\sigma_{//}/\sigma_{\perp}$ in this range was 450–550. This ratio is about one tenth of the value for highly oriented graphite block⁸⁾. The value of $\sigma_{//}$ in this HTT range is about ten times as large as that of alkaline metals, transition metals, and silicon. At HTT > 1600°C, $\sigma_{//}/\sigma_{\perp}$ increased again with raising HTT, though both $\sigma_{//}$ and σ_{\perp} increased. The $\sigma_{//}/\sigma_{\perp}$ for the 2800°C treated film was about 2×10^3 , which is the same order of magnitude with the values for graphite (3×10^3)

and highly oriented graphite block ($4\text{--}5 \times 10^3$)⁸⁾. The upward trend of $\sigma_{//}$ and σ_{\perp} in **Fig.1** suggests that the anisotropy will be more pronounced at HTT > 2800°C.

As shown in **Fig.2**, there was some resemblance between the XRD patterns of 1000 and 1600°C treated films. The peak around $2\theta = 25^\circ$ was broad and the carbon 10 peak was very weak by the reflection mode, but the carbon 10 and 11 peaks appeared clearly by the transmission mode. The results indicate the formation of turbostratic structure in these films, and reasonably explain the similarity of electric conductivities. The carbon 002 peak became sharp and strong with raising HTT from 1600 to 2200°C, in parallel with the increase of $\sigma_{//}/\sigma_{\perp}$. The XRD patterns by the transmission mode, however, were not very different between the films treated at 1600 and 2200°C. Graphitization of the film proceeded with raising HTT, and d_{002} decreased linearly from 0.35 nm at 1600°C to 0.3360 nm at 2400°C as shown in **Fig.3**. The 002 peak, however, remained in the transmission mode XRD pattern of 2400°C treated film (**Fig.2**). The 002 peak disappeared from the films treated at HTT \geq 2600°C, and the strong 100 and 110 peaks and weak 101 peak appeared. The lattice

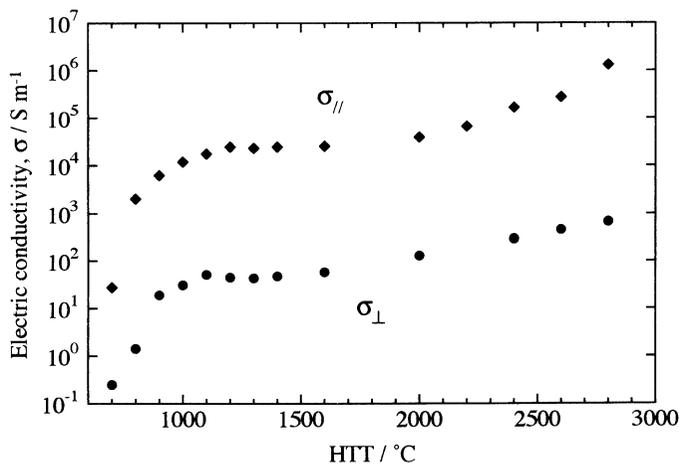


Fig.1 Electric conductivity parallel, $\sigma_{//}$, and perpendicular, σ_{\perp} , to the film surface as a function of HTT.

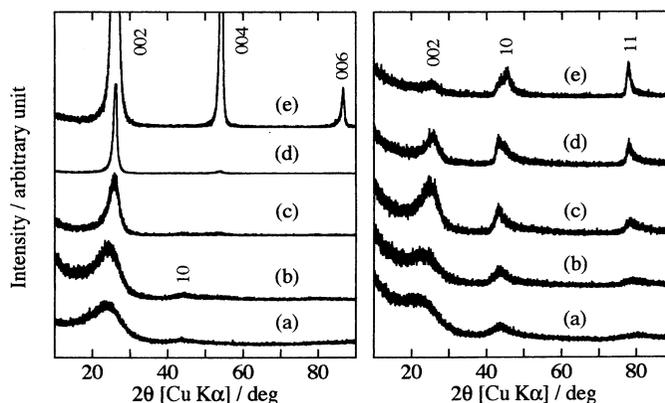


Fig.2 XRD patterns by (left) reflection and (right) transmission mode for films treated at (a) 1000, (b) 1600, (c) 2000, (d) 2200, and (e) 2400°C.

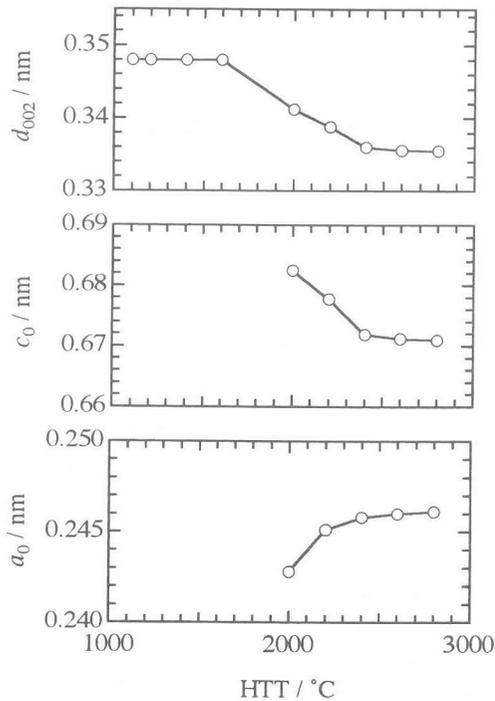


Fig.3 The average interlayer spacing, d_{002} , and the lattice constants, a_0 and c_0 , as a function of HTT.

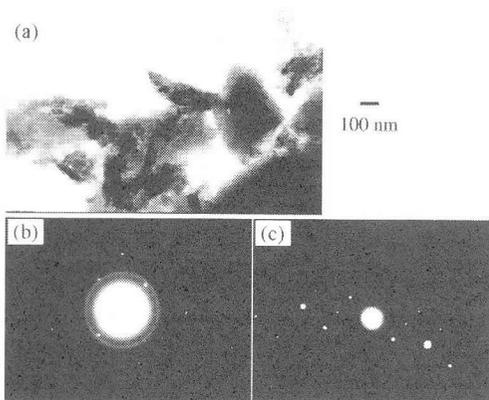


Fig.4 (a) TEM photograph, and (b) and (c) SAED patterns for the 1600°C treated film.

constants for the films treated at $\text{HTT} \geq 2000^\circ\text{C}$ are shown in **Fig.3**. The changes of d_{002} and c_0 with HTT are comparable to those reported for commercially available Kapton film³⁾, but a_0 was smaller even at $\text{HTT} = 2200^\circ\text{C}$. This is mainly due to poor molecular orientation of the laboratory-made film. The results shown in **Fig.3** indicate that the graphite structure is almost completed at $\text{HTT} > 2400^\circ\text{C}$, but the electric conductivities are still increasing with raising HTT (**Fig.1**).

By TEM, definite layered structure was not observed in the 1600°C treated film as shown in **Fig.4(a)**, but spotty patterns with rings were obtained by SAED in many parts of the film, as shown in **Fig.4(b)** and (c). These also suggest the formation of layered structure, and are consistent with the results by XRD, though the structure may be imperfect and not very large in size.

As shown above, the anisotropy of electric conductivity for carbonized polyimide films was observed at HTT as low as 700°C. Without the development of layered structure, such anisotropy should not occur. It may be concluded that, as expected, this is owing to the molecular orientation originally present in the film.

Acknowledgment

We thank Prof. Y. Kaburagi at Musashi Institute of Technology, for his help in the graphitization of polyimide films.

References

- 1) M. Inagaki, T. Takeichi, Y. Hishiyama, A. Oberlin, in: P. A. Thrower and L. R. Radovic (eds.), *Chemistry and Physics of Carbon*, Vol.23, Merce! Dekker, New York (1991) p.245-333.
- 2) M. Inagaki, T. Ibuki and T. Takeichi, *J. Appl. Polym. Sci.* **44** (1992) 521-525.
- 3) Y. Hishiyama, K. Igarashi, I. Kanaoka, H. Fujii, T. Kaneda, T. Koidesawa, Y. Shimazawa and A. Yoshida, *Carbon* **35** (1997) 657-668.
- 4) H. Konno, H. Oka, K. Shiba, H. Tachikawa and M. Inagaki, *Carbon* **37** (1999) 887-895.
- 5) H. Konno, K. Shiba, Y. Kaburagi, Y. Hishiyama and M. Inagaki, *Carbon* **39** (2001) 1731-1740.
- 6) L. J. van der Pauw, *Philips Res. Repts.* **13** (1958) 1-9.
- 7) JSPS 117 Committee, *TANSO* **1963** [No.36] 25-34 [in Japanese].
- 8) M. Murakami, N. Nishiki, K. Nakamura, J. Ehara, H. Okada, T. Kouzai, K. Watanabe, T. Hoshi and S. Yoshimura, *Carbon* **30** (1992) 255-262.