Graphitization behavior related to texture of Kapton-derived carbon film studied by Raman spectroscopy, X-ray diffractometry and Scanning electron microscopy

Akira Yoshida[A], *Yutaka Kaburagi*[B] *and Yoshihiro Hishiyama*[C]

[A]Advanced Research Laboratory, [B]Faculty of Engineering, [C]Professor Emeritus, Tokyo City University, 1-28-1 Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

Introduction

The first order Raman spectrum for carbon materials is useful for investigation of graphitization behavior because the full width at half maximum intensity of the G band, G-FWHM, is related to interlayer spacing d_{002} [1]. The absorption of light in carbon materials, however, is so large that the observed spectra are limited to a thin surface layer. In carbon materials, textures at the surface and interior are usually different. For study of graphitization of carbon materials at the surface with Raman spectroscopy, we must conduct the investigation together with those of SEM (scanning electron microscope) observation and X-ray diffraction. We investigate graphitization behavior related to texture for Kapton-derived carbon films through Raman spectroscopy, SEM microscopy and X-ray diffractometry.

Experimental

Samples were carbonized films derived from commercially available polyimide film Kapton of 25 μm in thickness. From a sheet of Kapton, the samples for carbonization cut into rectangles of appropriate size were carbonized at 900°C in a flow of high purity nitrogen gas [1]. The carbonized films were then heat-treated at temperatures of 2000, 2050, 2100 and 2200°C with residence times of 12, 20, 30, 45, 75, 90, 120, 150, 180 and 300 min at the highest temperatures [1]. We obtained film samples about 10 – 15 μm in thicknesses without cracks or pores. The samples are denoted hereafter by "KAP" followed by the numbers for the heat treatment temperature and heat treatment time, "KAP-2000-12" for example.

SEM observations were made for fractured surfaces of the samples. X-ray diffraction measurements were conducted for film samples. Mounting on a specially designed sample holder for films, with CuKα radiation the 004 lines were measured for samples in reflection, while the 110 lines were obtained in transmission using a rotating anode diffractometer. Pure $K\alpha_1$ intensity data were obtained by eliminating the $K\alpha_2$ component of the monochromated Cu-Kα radiation with the Rachinger procedure [2,3]. For 004 lines, the profiles were corrected for absorption, polarization, and the atomic scattering factor of carbon. The values of the interlayer spacing d_{002} and the crystallite size L_a were determined from the 004 and 110 lines, with reference to the 311 and 331 lines of high purity Si powder, respectively, as external standards. The Raman spectra of the samples were measured in air at room temperature with a 514.5 nm line of an argon laser as the incident radiation perpendicular to the incident plane, i.e. the sample surface [1].

Results and Discussion

Figure 1 shows a SEM micrograph of a fracture surface of the sample KAP-2050-12 by way of example. In the micrograph, a shiny band on the left is the image of the sample surface. Shining is due to the edge effect. We can see a gradual change of the texture from the surface to the inside. We could expect large differences in texture at the surface and deep inside, i.e. with increasing heat treatment time at a given heat treatment temperature the layer texture is developed at the surface while the development is a bit reduced in inside. Such a carbon film sample shows an unsymmetrical 004 diffraction profile which could be decomposed into two symmetrical component peaks as demonstrated for KAP-2050-12 in Fig. 2. The component related to the highest Bragg angle can be assigned to the diffraction from the surface. Since the Raman spectrum of carbon material is the spectrum of the scattered light from the topmost layer of the surface, the graphitization parameter of Raman spectra such as G-FWHM must be compared with X-ray graphitization parameters such as d_{002} obtained from the diffraction line with the highest Bragg angle.

Figure 3 shows the values of d_{002} obtained from the region related to the surface texture and interior of the KAP-2100 samples (a) and KAP-2200 samples (b) plotted as a function of heat treatment time, HTt. We assume that the threshold d_{002} value for graphite is 0.338 nm. The surface of the KAP-2100 sample graphitizes with HTts exceeding 150 min while the interior does not graphitize even after a 300-min treatment. On the contrary, KAP-2000 samples do not graphitize at the surface or interior after a 300-min treatment. On the other hand, the KAP-2200 sample graphitizes very well with HTts above 100 min. The d_{002} for graphitized samples, the samples with HTts above 100 min, are close to or a bit lower than 0.3360 nm; the value for the 300 min-treated sample being 0.3358 nm. For the KAP-2200 samples, the graphitization for interiors estimated from d_{002} is much lower than that for the surfaces. The graphitization degrees estimated from d_{002} for interiors of the KAP-2200 samples are much lower than those at the surfaces.

The values of G-FWHM are plotted as a function of d_{002} at the surface of the sample in Fig. 4. The G-FWHM values are scattered in the figure for the samples with $d_{002} \geq 0.341$ nm. In this d_{002} range, the values are found close to or on the vertical lines indicated in the figure, while for the samples with $d_{002} < 0.3341$ nm, G-FWHM is obtained without large scatter. An abrupt but small change in G-FWHM occurs at a d_{002} value around 0.3388 nm, which may be due to transformation from turbostratic structure to graphite, so the threshold d_{002} value for graphite at 0.338 nm assumed above appears quite reasonable. In contrast, the G-FWHM values for

the samples KAP-2000 and KAP-2050 are plotted as a function of $1/L_a$ in Fig. 5. $1/L_a$ seems to be a good parameter to relate to G-FWHM.

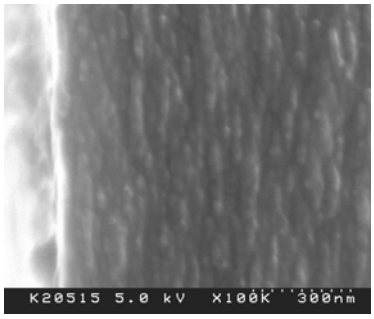

Fig. 1 SEM image of fracture surface of KAP-2050-12.

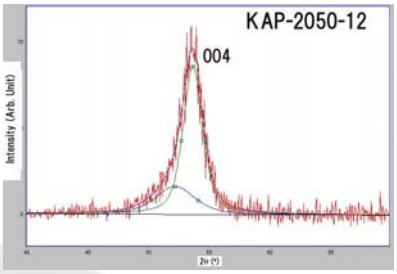

Fig. 2 Decomposition of 004 line for sample KAP-2050-12.

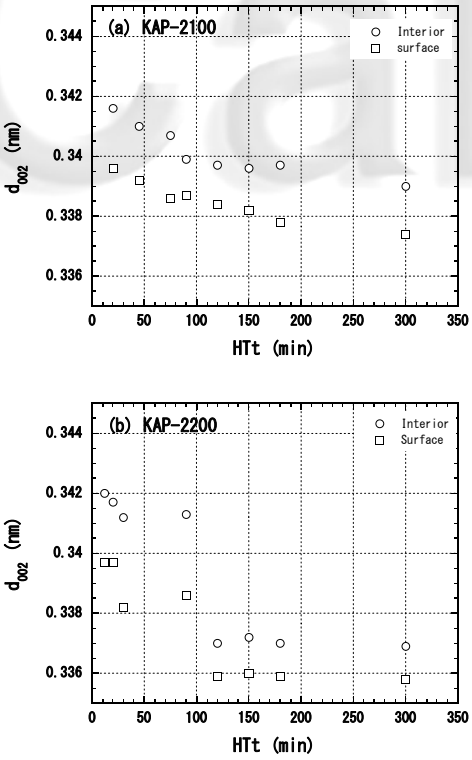

Fig. 3 d_{002} values for samples KAP-2100(a) and KAP-2200 (b) as a function of HTt.

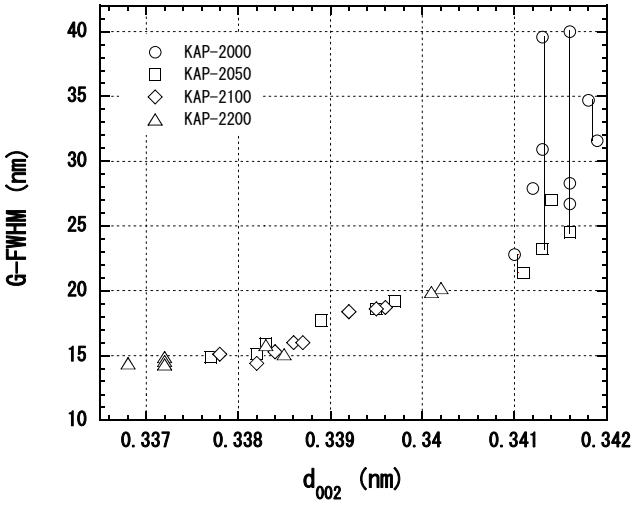

Fig. 4 G-FWHM of samples KAP-2000, -2050, -2100 and -2200 plotted as a function of d_{002} at the surface.

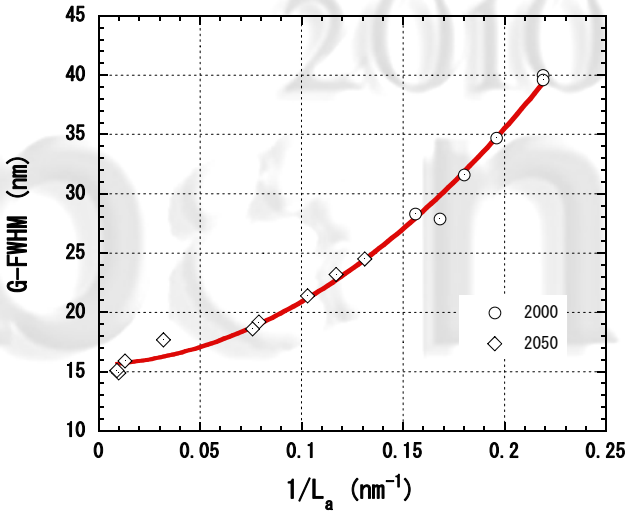

Fig. 5 G-FWHM of samples KAP-2100, -2050, -2100 and -2200 plotted as a function of $1/L_a$.

References

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