# LIBERATION OF NITROGEN ATOMS FROM TWO-DIMENSIONAL GRAPHITE LATTICE OF KAPTON-DERIVED CARBON

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## Introduction

Highly crystallized graphite films can be prepared from the carbonized films of commercially available polyimide film Kapton with a thickness of 25 μm (hereafter simply denoted by Kapton) by high temperature heat treatment at 3100-3200°C under atmospheric pressure of pure argon gas[1].

Microtexture of the Kapton-derived carbon film carbonized at 900°C is granular, similar to that of glass-like carbon[2]. The granular microtexture gradually elongates along the direction parallel to the specimen surface in a range of heat treatment temperature (HTT) between 1900 and 2200°C, and then suddenly changes to the layer microtexture similar to those of kish graphite and HOPG at HTT around 2300°C[2]. The sudden change in the microtexture corresponds to the initial stage of graphitization of the Kapton-derived carbon film. Kapton contains nitrogen atoms in its molecular structure, which was shown to remain in the Kapton-derived carbon film even after the heat treatment at temperatures above 2000°C[3]. Recently, Inagaki et al. found by X-ray photoelectron spectroscope (XPS) for the Kapton-derived carbon film that the nitrogen remains after heat treatment at 2200°C for 30 min and it does not exist after heat treatment at 2300°C for 30 min[4]. They concluded by theoretical calculation based on ab-initio molecular orbital theory that the nitrogen atoms are in tertiary bonding state and can be substituted into two-dimensional graphite lattice. We may assume that the nitrogen atoms remained deforms the graphene layers and the microtexture becomes granular. The departure of the nitrogen atoms causes to change the microtexture to the layer one.

The Kapton-derived carbon film heat-treated at 2200°C for 30 min has a turbostratic structure. The turbostratic structure changes to a graphitic one by heat-treatment at 2300°C for 30 min. It is supposed that at HTT of 2200°C the content of nitrogen atoms remained in the carbon film depends on heat-treatment time (HTt) and accompanies structural change. Therefore, in the present study, the liberation of nitrogen atoms at 2200°C was examined by measuring XPS and X-ray diffraction (XRD) as a function of heat-treatment time HTt.

## Experimental

The starting material used was a Kapton with 25 μm in thickness. It was cut into rectangular specimens of about 10 mm x 20 mm. They were carbonized in a flow of nitrogen gas at 900°C with a residence time of 1 hr at the top temperature by the method described in reference 2. The carbonized films were heat-treated at 2200°C also by the method described in reference 2. Treatment times at the top temperature were 12, 20, 30, 45, 75, 120 150, 180, and 300 min, respectively.

For the carbon films heat-treated, XRD measurements were carried out for film specimens with a cleaved thin HOPG as an external standard. For each film, the 004 diffraction was measured in reflection mode and the 110 in transmission mode. The interlayer spacing $d_{002}$ and crystallite thickness $L_c$ were determined from the 004 diffraction line and the crystallite diameter $L_a$ from the 110 line.

XPS measurement was made with SSX-100 of Surface Science Instruments for the carbon films. In a vacuum better than $10^{-7}$ Pa, monochromated X-rays (10 kV, 20 mA) irradiated each carbon film. XPS spectra of N1s and C1s electrons were measured with setting the electron take-off angle to 90°. Binding energies were corrected by referring to that of $Au4f_{7/2}$ electrons for a gold standard. For these carbon films, the nitrogen content is so small that a longer accumulation time for the counts in the measurement was needed. Scans of 300 times were used to obtain the spectrum. The integral intensities of N1s and C1s peaks were calculated by subtracting background intensities.

## Results and Discussion

The interlayer spacing $d_{002}$ is plotted as a function of HTt for the Kapton derived carbon films in Figure 1. Figure 2 shows plots of crystallite thickness $L_c$ and crystallite diameter $L_a$ against HTt. These results indicate that at 2200°C the crystal growth of the Kapton-derived carbon film is rapid up to HTt of 90 min and continue annealing out of crystalline defects. In Figure 3, N1s electron spectra for the carbon films heat-treated at HTt's of 20, 30,

45 and 180 min are shown. These spectra were obtained through the same experimental condition. Therefore, the intensity reflects the content of nitrogen atoms substituted into the two dimensional lattice. The content of the nitrogen atoms decreases with increasing HTt, i.e. with improvement of crystallinity. A trace of the N1s peak appeared for the carbon films with HTt's of 180 and 300 min, though the result for the latter is not shown. This fact suggests that the small fraction of the turbostratic region contained nitrogen atoms remains in the well-crystallized matrix of the carbon film heat-treated very long time at 2200°C.

## References


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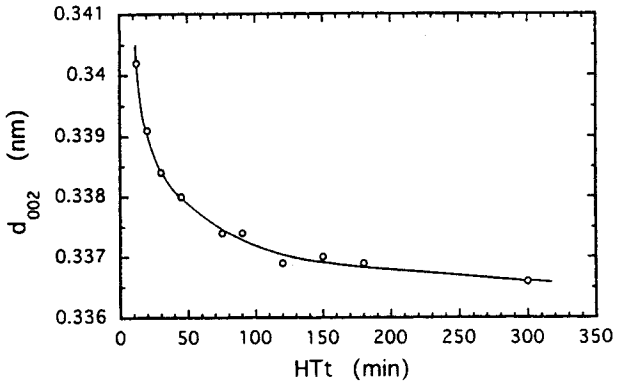


Figure 1. Interlayer spacing $d_{002}$ for Kapton-derived carbon film heat-treated at 2200°C plotted as a function of HTt.

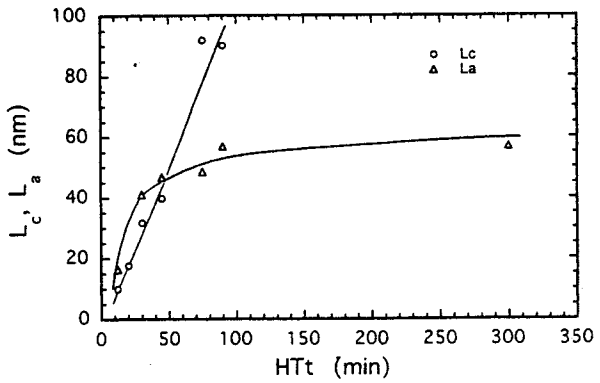


Figure 2. Crystallite thickness $L_c$ and crystallite diameter $L_a$ for Kapton-derived carbon film heat-treated at 2200°C plotted as a function of HTt.

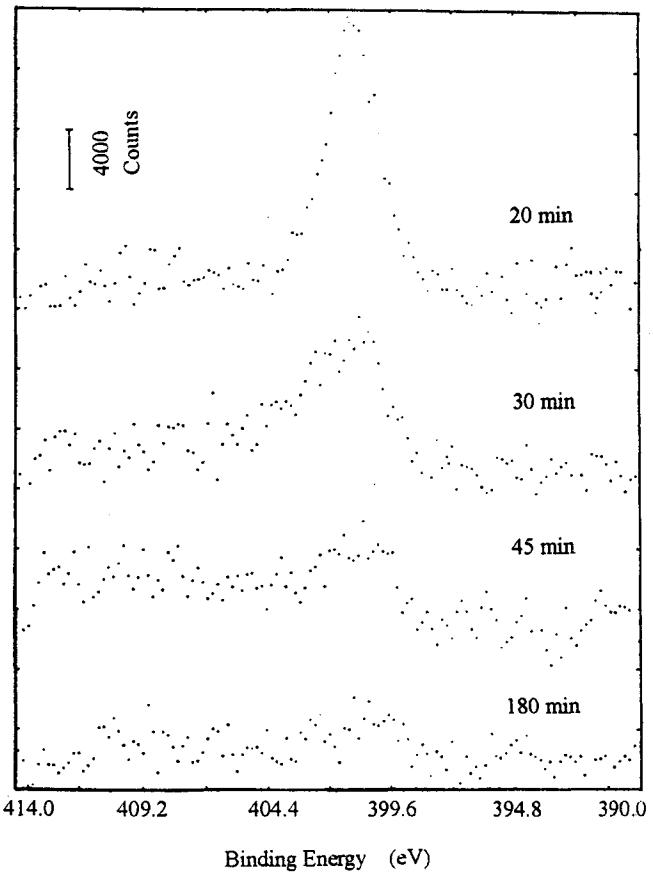


Figure 3. N1s electron XPS spectra for Kapton-derived carbon Film heat-treated at 2200°C with a parameter of HTt.