

GRAPHITE FILMS FROM POLYIMIDES II. STRUCTURAL CONTROL

M. Inagaki¹, T. Takeichi² and Y. Hishiyama³

¹ Faculty of Engineering, Hokkaido University, Sapporo, 060 Japan

² Toyohashi University of Technology, Toyohashi, 441 Japan

³ Musashi Institute of Technology, Setagaya-ku, Tokyo, 158 Japan

The well-crystallized graphite films were found to be prepared from polyimide films by a simple heat treatment in inert atmosphere with a slight pressure. The selection of starting imide molecules and heat treatment conditions for their carbonization and graphitization were studied in detail in order to have high quality graphite films; rigid imide molecules and high degree of their preferred orientation along the film surface, a suitable heating rate during carbonization and a holding at 2100–2300°C prior to higher temperature treatment were preferable. A constraint during imidization was reported to give high degree of graphitization which seemed to be due to the improvement of molecular orientation in films.

In order to obtain high quality graphite films from polyimides, the following factors have to be controlled; 1) flatness and rigidness of starting imide molecules, 2) high degree of orientation of the molecules along the film surface, 3) less bridging between molecules caused by the disturbance of molecular orientation in polyimide films, 4) less disturbance of molecular orientation during carbonization and graphitization due to the out-gas of non-carbon atoms. The former two are related to the precursor films, the selection of precursor imide molecules and the preparation condition of films. The latter two depend on the condition of carbonization and graphitization. Here, the control of these factors are discussed to obtain high quality of graphite films.

Flatness and rigidness of imide molecules

Imide molecules consist of two parts, imide part coming from starting anhydride and bridging part from diamine. The molecule PMDA/PPD in Table 1 is known to be flat, where all constituent atoms are on a plane, and rigid. The molecule PMDA/ODA is shown by a structural analysis to be also flat, except

a kink at the etheric oxygen in its bridging part. The molecule BTDA/DABP, on the other hand, is easily supposed to have steric arrangement of constituent atoms at carbonyl groups in imide and bridging parts. These three molecules are main component in three commercially available films named PPT, Kapton and Larc-TPI, respectively. In addition, the molecular structure containing two kinds of bridging part which consists of a commercial film Novax is shown in Table 1. The magnetoresistance value, a measure of graphitization degree, for each films after heat treatment at either 3100 or 3200 °C is also listed in Table 1. It has to be pointed out that the film Larc-TPI which consist of steric molecules has very low degree of graphitization, though other films are comparable.

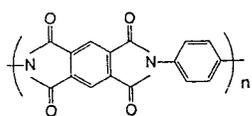
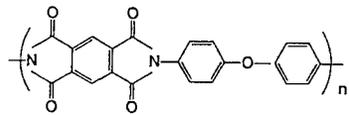
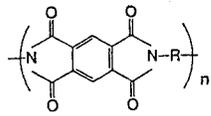
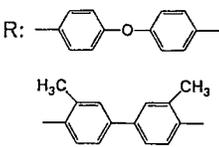
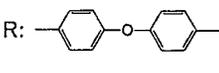
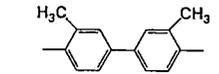
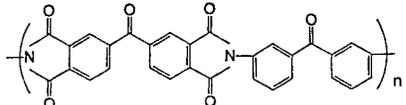
The results show that the selection of the molecular structure of starting polyimide films is very important to obtain high quality graphite film, though the other factors also have a strong effect on the development of graphitic structure in the resultant films. It is also worth while to mention that thin film of glass-like carbon is also possible to obtain from some polyimides.

Molecular orientation in films

The preferred orientation of these imide molecules in the film was seen to govern the graphitization degree of the resultant carbon films after the heat treatment at high temperatures as 3200°C.

We experienced that even using the molecules of PMDA/ODA the laboratory-made films gave much lower graphitization degree than the commercial Kapton film. This was supposed to be due to the difference in orientation degree of molecules; in the laboratory only small constraint during imidization was given, but the commercial film experienced high degree of constraint during imidization in order to prepare homogeneous and

Table 1 Molecular structure of imides and magnetoresistance of corresponding commercial films after heat treatment at 2800-3200°C.

Molecular structure	commercial film	$(\Delta\rho/\rho)_{\max}$ (%)
 PMDA/PPD	PPT	1205
 PMDA/ODA	Kapton	606.3
 PMDA/ODA + OTD	Novax	1191
 R:  	Larc-TPI	0.554
 BTDA/DABP		

thin films.

We showed that uniaxial stretching for the imide films was not preferable to have high degree of plane orientation and consequent high degree of graphitization (this conference).

The thickness of starting polyimide films was found to influence on the graphitization, which was also explained on the basis of preferred orientation of imide molecules during film preparation, thin film giving high degree of crystallinity and thick one low degree, particularly at the center of film.

Carbonization and graphitization conditions

The heating rate during carbonization of polyimide films was found to be important to get high degree of graphitization[6]. In Fig. 1, maximum magnetoresistance value after 3000°C-treatment is plotted against residence time at the temperature range between glass transition and decomposition temperatures, short residence time corresponding to high heating rate, on two films, Kapton and Novax with the thickness of 25 μm.

Slow heating is reasonably supposed to result in slow departure of non-carbon atoms and, as a consequence, in less disturbance of molecular orientation in the film. The result on Kapton is consistent

with this mechanism, but the decrease in graphitization degree in the range of long residence time observed on Novax, as shown in Fig. 1, can be explained by the twisting at the bi-phenyl bond in the bridging part OTD above glass transition temperature. The conformational change in polyimide films is also important factor to control the crystallinity of the films.

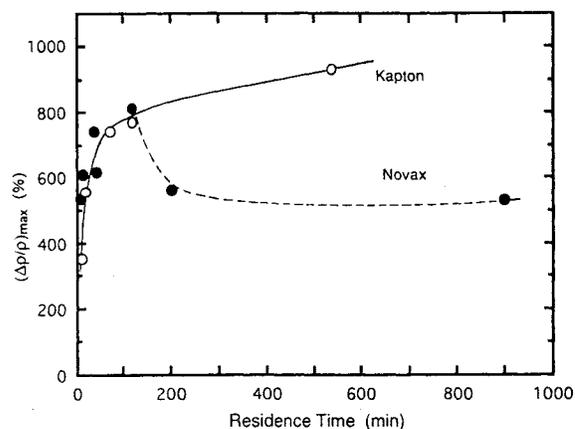


Figure 1 Changes of magnetoresistance with residence time on two polyimide films