EFFECT OF COLD-DRAWING ON GRAPHITIZATION OF POLYIMIDE FILMS

T. Takeichi[1], Y. Kaburagi[2], Y. Hishiyama[2] and M. Inagaki[3]

[1] Toyohashi University of Technology, Toyohashi, 441 Japan
[2] Musashi Institute of Technology, Setagaya-ku, Tokyo, 158 Japan
[3] Faculty of Engineering, Hokkaido University, Sapporo, 060 Japan

INTRODUCTION

Most of polyimide films have been known to be good precursors for obtaining graphite films through a simple heat treatment procedure. 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. The cold drawing of polyamic acid films was thought to be one of effective techniques for improving the molecular orientation. In our previous works[1,2], the electrical conductivity along the film surface was found to increase with the increase in draw ratio on polyamic acid films after the carbonization at 1000°C, more pronounced on rigid molecules than on flexible molecules of polyimides.

In the present work, the films drawn with different ratios were heat-treated up to 2800°C and the effect of cold-drawing on the development of graphite structure in the films was examined.

EXPERIMENTAL

Two precursor polyimides were selected, BPDA/PDA for rigid polymer and PMDA/ODA for flexible polymer. Molecular structures of these imides are shown in Fig. 1.

The polyamic acids, which were prepared from respective diamine and dianhydride in a solution and casted on a glass substrate, were cold-drawn after peeling off the glass plate by stretching in different degrees at room temperature. The imidization of these polyamic acid films were performed by a stepwise heating up to 300°C. For comparison, the polyamic acid films were also imidized on the glass substrate by the same heating procedure.

The polyimide films thus prepared were carbonized at 1000°C for 1 hour in nitrogen flow. The carbonized films were subjected for the graphitization; by sandwiching in between two high-density graphite blocks with polished surfaces, heating up to 2800°C with a heating rate of 200°C/h and kept at the temperature for 30 min in a flow of argon.

On the graphitized films, magnetoresistance parameters, $(\Delta\rho/\rho)_{max}$, $(\Delta\rho/\rho)_{TLmin}$ and $(\Delta\rho/\rho)_{Tmin}$, were measured at liquid nitrogen temperature under a magnetic field strength of 1 tesla.

The rocking curves for 002 planes in the graphitized films were determined at room temperature and a mosaic spread (MS) was determined as a measure of orientation.

RESULTS AND DISCUSSION

The magnetoresistance and X-ray data on the graphitized films are summarized in Table 1. In the table, the change in film thickness during graphitization, Δt, is also shown, because it has been pointed out to be one of the measures for the degree of graphitization of the film.

The magnetoresistance data in Table 1 show that the graphitization in the films is hindered with the increase in draw ratio. In our previous works[1,2], a linear increase in electrical conductivity of the carbonized films with the increase in draw ratio was observed, more pronounced on the polyimides of rigid molecule as BPDA/PDA than on those of flexible molecule as PMDA/ODA. Based on these previous works, we were expecting certain acceleration of graphitization in the cold-drawn films. The present results show, however, that it is not the case in both rigid and flexible polymers. On the film of BPDA/PDA, a remarkable decrease in $(\Delta\rho/\rho)_{max}$ is observed with the increase in draw ratio, becoming even negative value by more than 20 % drawing. On PMDA/ODA, the same decrease in $(\Delta\rho/\rho)_{max}$ is confirmed. A low degree of graphitization is confirmed by d_{002} value on the 21.7%-drawn BPDA/PDA film after graphitization. The reduction of film thickness Δt with 2800°C-treatment becomes smaller with the increase in draw ratio, being consistent with low degree of graphitization in the cold-drawn films.

The change in orientation of graphite layers parallel to the surface in the cold-drawn films was directly indicated from the rocking curves measured. The curve measured on the 21.7%-drawn film was so much broadened, in comparison with that of the 0%-drawn film. This change in orientation of graphite layers is evaluated by a mosaic spread(MS)-value of the rocking curves and summarized in Table 1.

The cold-drawing of polyamic acid films was found to hinder the graphitization of the resultant carbon films. For this hindrance in graphitization, the change in orientation scheme of graphite layers in the films due to the cold-drawing seems to be responsible. In the drawn films, the component of axial orientation of graphite layers is mixed in the original scheme of plane orientation in the graphitized films derived from polyimides. This disturbance in orientation of graphite layers in the graphitized films is reasonably supposed to be due to the change of preferred orientation of polyamic acid molecules during cold-drawing.

During carbonization of polyimide films, a large amount of non-carbon atoms are released as gases and basic structural units of graphite-like carbon layers are established. In the films with a high degree of plane orientation, for example the film imidized on the glass, it has been shown by our works that very extended carbon layers are easily formed by heat treatment and resulted in well-crystallized graphite films. In the films with less degree of plane orientation of polyamic acid molecules, containing axial component, however, the formation of large carbon layers seems to be hindered due to not only small thickness of the film, but also the formation of cross-linking between neighboring molecules on the course of carbonization. Therefore, the low degree of graphitization of the films derived from the cold-drawn polyamic acid films is the results of the increase of axial mode in orientation scheme and also of the cosequent formation of cross-linking.

References

1. T.Takeichi, H.Takenoshita, S.Ogura and M. Inagaki, Chem.Lett., 1993, 657 (1993).
2. T.Takeichi, H.Takenoshita, S.Ogura and M. Inagaki, J.Appl.Polym.Sci.,54,361(1994).

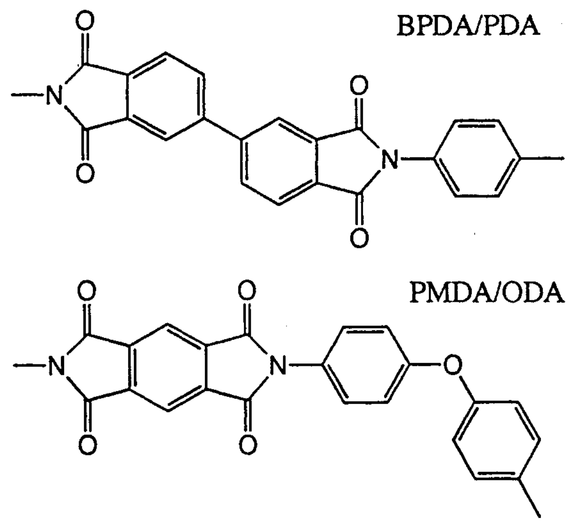

Figure 1 Molecular structures of polyimides

Table 1 Magnetoresistance and X-ray parameters of the films

Polyimide	Imidization conditons	$(\Delta\rho/\rho)_{max}$ (%)	Δt (%)	d_{002} (nm)	MS (°) Tl	MS (°) T
BPDA/PDA	0% drawing	285	52	0.3355	6.8	4.2
	2.87% drawing	207	55			
	21.7% drawing	- 0.49	34	0.3396	11	39
	on glass	333	58	0.3355	5.7	2.3
PMDA/ODA	0% drawing	59.4	69			
	25.9% drawing	- 0.34	41			
	on glass	69.8	64			