LASER MICROSCOPIC OBSERVATION OF OXIDATION BEHAVIOR OF POLYIMIDE FILM DOPED WITH BORON

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Introduction

A thin film of polyimide, Kapton, gives a carbon film with highly graphitizing nature [1-2]. Boron doping is known to affect graphitization and to improve oxidation resistance of carbonaceous materials [3-4]. In the present work, the effect of boron addition on graphitizability and oxidation behavior of the heat-treated films was studied by the measurement of the lattice parameter of graphite and mass loss at elevated temperatures. Morphological changes with oxidation process was investigated by a in-situ observation laser microscope for the heat-treated film, and by paying special attention to the influence of boron doping into the film on oxidation behavior.

Experimental

Polyimide films used were commercial Kapton films with 25 μm in thickness and 30 x 30 mm in size. Boron was deposited on the polyimide film by PVD method under 10^{-4} Torr. The B-deposited and no deposited films were heat-treated at 1000°C in N_2 gas for carbonization, and then heat-treated at 2000° and 2500°C for 1 hr in Ar gas (B-doped films specimens are named B20 and B25 respectively, N20 and N25 are the non-doped one.). X-ray diffraction (XRD) patterns were obtained using CuKα radiation for all pulverized specimens, and the interlayer spacing d(002) and crystallite size Lc(002) were determined by referring to an internal standard of silicon. The specimens were cut into piece with 3 x 3 mm in size for oxidation tests. For the oxidation test, the piece was mounted in alumina crucible in a thermogravimetry analyzer (TGA) and laser microscope (LM). The mass loss and the morphological changes were recorded by a computer and video cassette recorder as a function of temperature at constant heating rate (10°C/min) in flowing air (100ml/min).

Results and Discussion

Figure 1 shows change of d(002) and Lc(002) for the films heat-treated at 2000 and 2500°C with content of boron deposited. The d(002) value decreased with an increase of boron content. This suggests two reasons that boron accelerated graphitization of the films and boron dissolved in graphite at substitutional position [3]. From the values of Lc(002), B caused a growth in crystallite size of graphite for the films heat-treated at 2000° and 2500°C. These results indicate that ordering of graphite crystal structure of the films was promoted by B-doping.

TGA curves of the films with and without B-doping are shown in Fig. 2. The B-doped film heat-treated at 2000°C (B20) showed higher oxidation resistance than that of the film without B-doping (N20). The heat treatment at 2500°C improved oxidation resistance of

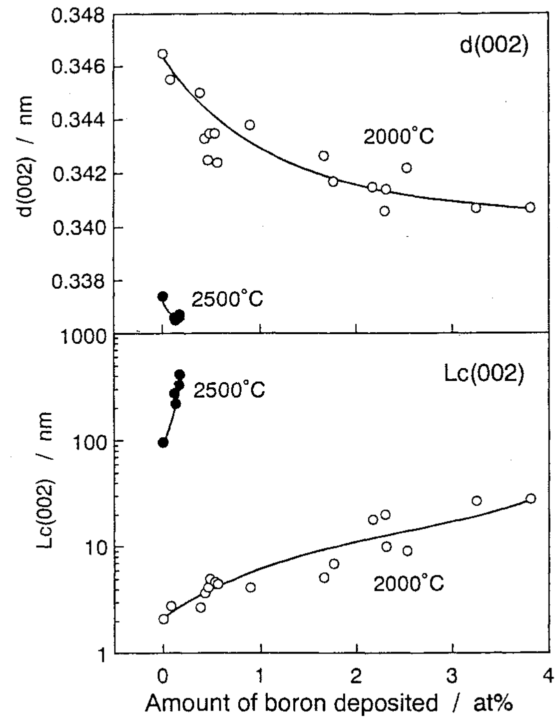

Fig. 1. Change of d(002) and Lc(002) for the films heat-treated at 2000° and 2500°C with amount of boron deposited.

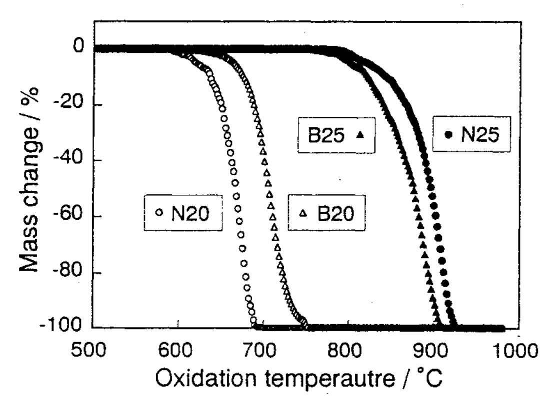

Fig. 2. TGA curves of the films with and without B-doped heat-treated at 2000° and 2500°C.

the films caused by growth of graphite crystallite. On the other hand, B-doping degraded oxidation resistance of the films heat-treated at 2500°C.

From the LM observation, morphological changes of the films heat-treated at 2000°C started at 520°C for N20 and at 570°C for B20, and the difference of morphological change between them was not clear. In the case of the films heat-treated at 2500°C, the morphological changes of the N25 started at 690°C with growth of oxidation pits like a coin and the B25 started at 650°C with growth of dimples. These phenomena suggests that oxidation of N25 proceeded with preferentially parallel to c-plane, and that of B25 proceeded from surface to the inside with isotropically (three dimensionally).

Figure 3 shows LM in-situ observation and illustration of morphological changes in the process of oxidation at 600°C for the film heat-treated at 2000°C. This film had a boundary between B20 region and N20 region in a film. The morphological changes of the film started at 520°C in the N20 region, and then start at 580°C in the B20 region. The oxidation proceeded remarkably in the N20 region near by the boundary. This suggests that graphite structure of the N20 region near by the boundary have been disordering by boron atom diffusion from B20 region.

Orientation of graphite 002 plane of the film heat-treated at 2500°C are shown in Fig. 4. The profile of B-doped film were broader than that of the no-doping film. It was found that the preferred orientation of the c-plane of graphite layers in the graphite films was degraded by 2500°C B-doping.

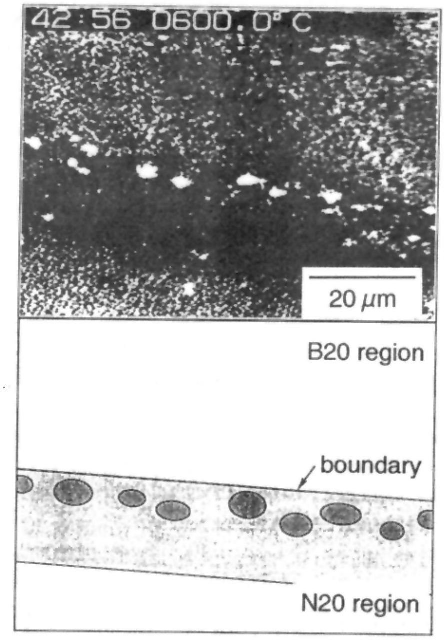

Fig. 3. LM in-situ observation and illustration of morphological changes in the process of oxidation at 600°C for the film heat-treated at 2000°C.

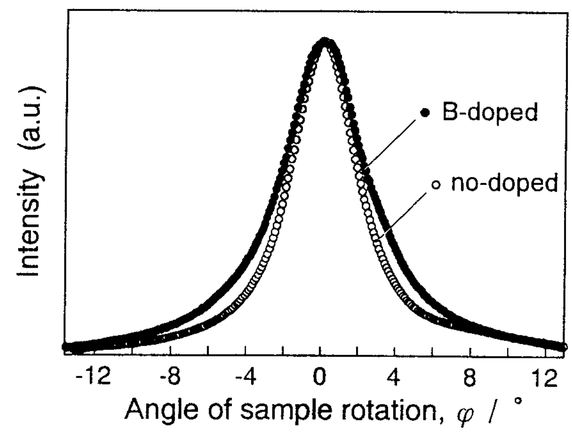

Fig. 4. Orientation of graphite 002 plane of the film heat-treated at 2500°C ; the angle φ is referred to the normal to the specimen surface at the diffraction angle giving the 002 intensity maximum.

Conclusions

The graphite crystal structure of the films was ordered by B-doping heat-treated at 2000° or 2500°C.

The B-doped film heat-treated at 2000°C showed higher oxidation resistance than those of the film without B-doping. On the other hand, B-doping degraded oxidation resistance of the films heat-treated at 2500°C.

From the in-situ observation, oxidation of the films heat-treated at 2500°C with no-doped proceeded with preferentially parallel to c-plane. Oxidation of the B-doped one proceeded from surface to the inside with isotropically (three dimensionally). These phenomena were thought to be caused by the graphite structure have been disordering by boron atom diffusion, and the preferred orientation of the c-plane of graphite layers in the heat-treated films was degraded by B-doping.

Acknowledgments

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