

# Ion-Beam-Induced Dual-Tone Imaging of Polyimide via Two-Step Imidization

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Dual-tone images in polyimide (Kapton) films were prepared by ion beam irradiation of partially imidized polyamic acid (PAA) films followed by alkaline etching in aqueous tetramethylammonium hydroxide (TMAH) solution. The treated films were heated at a final time for thermal stability. In partially imidized PAA films prepared at 150 °C, ion beam irradiation produced a negative hemispheric structured image with 1.0- $\mu$ m height and 1.5- $\mu$ m diameter. In contrast, a positive hole pattern with 0.3- $\mu$ m diameter appeared on the partially imidized PAA film prepared at 145 °C. By determination of the precise imidization degree of precursor polymer films on the basis of adsorption strength of an imide ring C–N bond (1380  $\text{cm}^{-1}$ ) in an attenuated total reflection infrared (ATR–IR) spectrum, it was revealed that the image mode of the films switches within a narrow range of imidization degree; positive and negative images were obtained from the PAA films with 67–83% and 89–94% imidization degrees, respectively.

## Introduction

Ionizing radiation sources such as ion and electron beams have attracted a great deal of attention as promising tools for nanofabrication of electronic devices of the next generation, as the beams can be focused to a diameter <1 nm and scanned to produce any design at high scanning speeds. The ionizing radiation is superior to optical lithography, which has limited resolution due to its wavelength.<sup>1–7</sup> Among the types of ionizing radiation, ion beam radiation has unique characteristics for nanoscopic fabrication: an ion beam deposits its energy to the substrate in a region <10 nm in diameter; the depth of the affected region can be controlled by changing the energy and kind of ion

particles. The most typical application of ion-beam-induced fabrication of a polymer film is the creation of “ion track membranes”, which possess cylindrical through-holes with diameters ranging from 10 to 100 nm.<sup>7–13</sup> The ion track membranes are easily prepared by ion beam irradiation, which causes scission of polymer main chains in a localized area. The damaged area of the film is then etched out. However, most ion track membranes are made of poly(ethylene terephthalate) (PET) or polycarbonate (PC), which do not possess sufficient thermal stability for microelectronic devices.

We herein introduce the precursor method to obtain thermally stable ion track membranes made of polyimides. As shown in Figure 1, the precursor method has two steps: (1) preparation of an ion track membrane by ion beam irradiation of partially imidized polyamic acid (PAA), followed by alkaline etching, and (2) transformation of the ion track membranes into thermally stable ion track polyimide membranes by heat curing. We foresaw two significant advantages in the precursor method. First, since the radiation sensitivity of polymers

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(1) Sheats, J. R.; Smith, B. W. In *Microlithography. Science and Technology*; Marcel Dekker: New York, 1998.

(2) Tagawa, S.; Nagahara, S.; Iwamoto, T.; Wakita, M.; Kozawa, T.; Yamamoto, Y.; Werst, D.; Trifunac, A. D. *Proc. SPIE* **2000**, 3999, 204.

(3) Nagahara, S.; Sakurai, Y.; Wakita, M.; Yamamoto, Y.; Tagawa, S.; Komuro, M.; Yano, E.; Okazaki, S. *Proc. SPIE* **2000**, 3999, 386.

(4) Matsui, S.; Kojima, Y.; Ochiai, Y.; Honda, T. *J. Vac. Sci. Technol.* **1991**, B9, 2622.

(5) Kubena, R. L.; Ward, J. W.; Stratton, F. P.; Joyce, R. J.; Atkinson, G. M. *J. Vac. Sci. Technol.* **1991**, B9, 3079.

(6) Sundararajan, N.; Keimel, C. F.; Bhargava, N.; Ober, C. K.; Opitz, J.; Allen, R. D.; Barclay, G.; Xu, G. *J. Photopolym. Sci. Technol.* **1999**, 12, 457.

(7) Spohr, R. *Ion Tracks and Microtechnology: Principles and Applications*; Vieweg & Sohn Verlagsgesellschaft mbH: Braunschweig, 1990.

(8) Peng, L.; Apel, P. U.; Maekawa, Y.; Yoshida, M. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2000**, 168, 527.

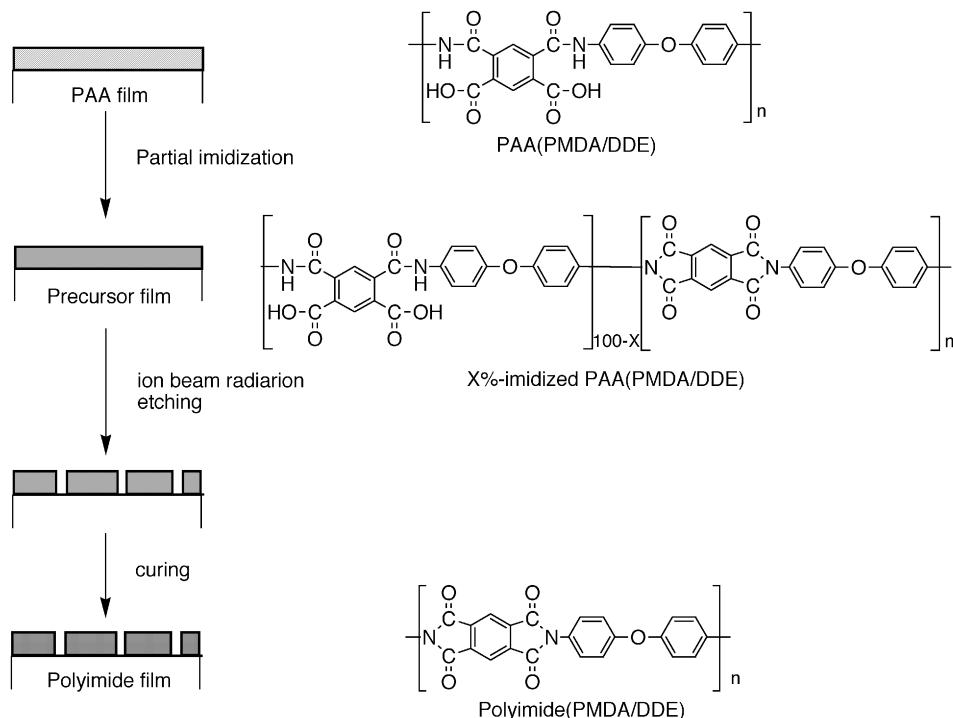
(9) Yoshida, M.; Asano, M.; Safranj, A.; Omichi, H.; Spohr, R.; Vetter, J.; Katakai, R. *Macromolecules* **1996**, 29, 8987.

(10) Reber, N.; Spohr, R.; Wolf, A.; Omichi, H.; Tamada, M.; Yoshida, M. *J. Membr. Sci.* **1998**, 140, 275.

(11) Spohr, R.; Reber, N.; Wolf, A.; Alder, G.; Ang, V.; Bashford, C. L.; Pasternak, C. A.; Omichi, H.; Yoshida, M. *J. Contr. Release* **1998**, 50, 1.

(12) Apel, P.; Schulz, A.; Spohr, R.; Trautmann, C.; Vutsadakis, V. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1998**, 146, 468.

(13) Dorschel, B.; Hartmann, H.; Kadner, K. *Radiat. Meas.* **1996**, 26, 51.



**Figure 1.** Schematic illustration of a precursor method for ion beam imaging of polyimide films with the chemical structures.

appears to be inversely related to their chemical and thermal stability, then PAA, a precursor of polyimide with low chemical and thermal stability, should be more sensitive to ion beam irradiation than the corresponding polyimides. Second, the sensitivity of PAA films can be controlled by changes in the imidization degree of the films because the extent of imidization in the precursor polymer determines alkaline solubility, which is one of the most important properties for sensitivity of polymer films to beam irradiations.<sup>14–20</sup>

There has been only one report of the preparation of an ion track membrane with Kapton (a commercial polyimide film), and that trial was with an oxidative etchant. Thus, we chose Kapton film to compare our alkaline etching method with the oxidative etching method for preparation of polyimide ion track membranes.<sup>21–24</sup> Surprisingly, we obtained negative images in the polyimide films when they were irradiated with  $^{129}\text{Xe}^{23+}$  ion beams, followed by alkaline etching. In this report we describe the relation between image mode (i.e., positive or negative) of the obtained films and the

imidization degree of the polyimide precursor, which was precisely determined using attenuated total reflection infrared (ATR-IR) spectroscopic analysis.

## Experimental Section

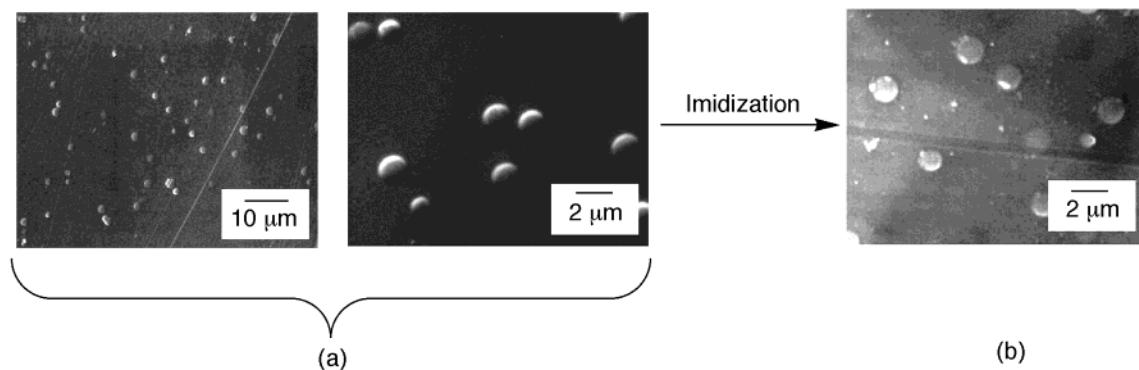
**Materials.** Pyromellitic dianhydride (PMDA) was purchased from Tokyo Chemical Industry Co., Ltd., recrystallized from 1,4-dioxane, and dried at 180 °C in vacuo for 10 h. 4,4'-Diaminodiphenyl ether (DDE) was purchased from Tokyo Chemical Industry Co., Ltd., recrystallized from ethanol, and dried at 60 °C in vacuo for 4 h. *N*-Methyl-2-pyrrolidinone (NMP) was purchased from Tokyo Chemical Industry Co., Ltd., and was dried over molecular sieves 4A.

**Measurement.**  $^1\text{H}$  NMR spectra were recorded on a JEOL GSX270W NMR spectrometer in dimethyl sulfoxide- $d_6$  as the solvent and the internal standard. Molecular weight was determined by a calibration based on gel permeation chromatography (GPC). The chromatogram was recorded using Shodex KD-804 and KD-805 columns eluted with a mixture of tetrahydrofuran/*N,N*-dimethylformamide (50/50 v/v) with phosphoric acid (0.6 mmol/L)/lithium bromide (0.6 mmol/L) at 40 °C at a flow rate of 1.0 mL/min. The number- and weight-average molecular weights of the polymers ( $M_n$  and  $M_w$ ) were determined on the basis of a standard polystyrene calibration. Infrared spectra were recorded on a JASCO FT/IR-5300 spectrometer. ATR-IR spectra were recorded on the FT/IR-5300 spectrometer attached ATR-500/M (ZnSe crystal). Film thickness was measured using a Mitutoyo SURFTEST SV-600 surface profiler. Contact angles were measured with a Kyowa CA-A contact angle meter. X-ray (Cu  $\text{K}\alpha$ ) diffraction analysis was undertaken with a Rigaku CN 2013 spectrometer.

**Preparation of Polyamic Acid and Its Partially Imidized Film.** PAA was prepared by a ring-opening polyaddition reaction of PMDA with DDE in NMP at room temperature according to a conventional method.<sup>25</sup> The resulting polymer solution was poured into a large amount of water to give a yellow powder of PAA in a 77% yield. The number- and weight-average molecular weights of the PAAs obtained were 24 000

- (14) Sroog, C. E.; Endrey, A. L.; Abramo, S. V.; Berr, C. E.; Edwards, W. M.; Olivier, K. L. *J. Polym. Sci. A* **1965**, *3*, 1373.
- (15) Dammel, R. In *Diazonaphthoquinone-Based Resists*; SPIE Optical Engineering Press: Washington, 1993; p 70.
- (16) Tsiartas, P. C.; Flanagan, L. W.; Henderson, C. L.; Hinsberg, W. D.; Sanchez, I. C.; Bonnecaze, R. T.; Willson, C. G. *Macromolecules* **1997**, *30*, 4656.
- (17) Owen, G. *Rep. Prog. Phys.* **1985**, *48*, 795.
- (18) Matsumoto, T.; Feger, C. *J. Photopolym. Sci. Technol.* **1998**, *11*, 231.
- (19) Maekawa, Y.; Miwa, T.; Okabe, Y.; Rames-Langlade, G.; Ueno, T. *Macromol. Rapid Commun.* **2000**, *21*, 35.
- (20) Maekawa, Y.; Miwa, T.; Okabe, Y.; Rames-Langlade, G.; Ueno, T. *Macromolecules* **2000**, *33*, 6794.
- (21) Tian-cheng, Z.; Brandt, R.; Vater, P.; Vetter, J. *Nucl. Tracks. Radiat. Meas.* **1988**, *15*, 771.
- (22) Vater, P. *Nucl. Tracks Radiat. Meas.* **1988**, *15*, 743.
- (23) Trautmann, C.; Bruchle, W.; Spohr, R.; Vetter, J.; Angert, N. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1996**, *111*, 70.
- (24) Trautmann, C.; Bouffard, S.; Spohr, R. *Nucl. Instr. Methods Phys. Res., Sect. B* **1996**, *116*, 429.

- (25) Bessonov, M. I.; Koton, M. M.; Kudryavtsev, V. V.; Laius, L. A. In *Polyimides, Thermally Stable Polymers*; Consultants Bureau: New York, 1987.



**Figure 2.** SEM photographs of (a) the negative image on the PAA film heated at 150 °C (89% imidized PAA) followed by irradiating with  $^{129}\text{Xe}^{23+}$  ion beam and etching in aqueous 5% TMAH solution at 40 °C for 1 h and (b) the corresponding polyimide film with curing at 350 °C for 1 h.

and 36 000, respectively. A 25 wt % dimethylformamide solution of the powder was spin-coated on a glass plate (50 × 1 mm) at 2000 rpm for 30 s.

For the clarification of the relationship between imidization temperature and the dissolution rate, the films were prebaked at 60 °C for 6 h in vacuo and then heated at a temperature ranging from 110 to 300 °C for 1 h on an Iuchi P-DHP hot plate. Here, the dissolution rate of the film denotes the rate of decreasing thickness of the film. The dissolution rates of the films were estimated by the ratio of the decreasing thickness (μm) of the films to the time required for dissolution in aqueous 15% TMAH solution at 30 °C. The samples for imaging experiments were prebaked at 70 °C for 6 h in vacuo and then baked at 100 °C for 2 h on a hot plate. The PAA films were then heated at a temperature ranging from 120 to 300 °C for 1 h on a hot plate to give partially imidized PAA films with 8–10-μm thickness. After the film was baked above 140 °C, many voids were observed on the surface. Therefore, in the case when the imidization temperatures were higher than 140 °C, the films were baked at 130 °C for 2 h and heated at a temperature ranging from 140 to 300 °C for 1 h on a hot plate to give partially imidized PAA films with a smooth surface without void formation.

**Ion Beam Irradiation and Patterning Evaluation.** Six sheets of film samples were set on the turntable-type film carrier in a vacuum chamber for the formation of ion-track pores in the film, which is connected to the Azimuthally Varying Field (AVF) cyclotron on the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA), Japan Atomic Energy Research Institute (JAERI), Japan.  $^{129}\text{Xe}^{23+}$  ion beams with an energy of 3.5 MeV/n were used with fluences of  $3 \times 10^7$  or  $1 \times 10^{10}$  ions/cm<sup>2</sup>. The irradiated films were etched in 1%, 5%, 10%, and 15% aqueous tetramethylammonium hydroxide (TMAH) solution at 40 °C without stirring. The specimens were washed with a large amount of water and dried at room temperature. The surfaces of the films were coated with gold using a Giko IB-3 ion coater and observed with a JEOL JXA-733 scanning electron microscope (SEM).

## Results and Discussion

**Imaging of Partially Imidized Polyamic Acid (PAA) Films.** The PAA film was heated at 150 °C to partially imidize the polyamic acid. The imidization degree of the PAA film was determined to be 89% according to the method described later. The film was irradiated with a  $^{129}\text{Xe}^{23+}$  ion beam, followed by etching in aqueous 5% TMAH solution at 40 °C for 1 h. A hemispheric structure with 1.0-μm height and 1.5-μm diameter was clearly observed on the film surface as shown in Figure 2a. The density of the hemispheric pattern was  $1.5 \times 10^6 \text{ cm}^{-2}$ , which was somewhat lower than the accumulated ion fluence of  $3.0 \times 10^7 \text{ ions/cm}^2$ .

The lower density of the hemisphere implies that the patterns should be formed only in the region where two or more ion tracks overlapped because a change in polymer structures induced by a single  $^{129}\text{Xe}^{23+}$  ion with an energy of 3.5 MeV/n is insufficient for the formation of the hemispheric pattern. The hemispheric pattern formation means negative imaging of the film, resulting from the gradient decrease of the dissolution rate in the region of 0.75 μm from the ion track center; the closer to the center, the lower the dissolution rate. The reason for decreasing the dissolution rate of the film should be cross-linking of the polymers (vide infra). The larger diameter of the hemisphere (1.5 μm) than that of hole patterns in conventional ion track membranes should be explained by two possible reasons: (1) the reactive species (such as radicals and free electrons) generated by energy deposition from  $^{129}\text{Xe}^{23+}$  ions diffuse through the polyimide backbone with the aid of the formation of a charge-transfer complex and (2) the hemispheric structure with larger diameter is visualized as the result of amplification of a slight amount of cross-linking of polymer chains during the etching procedure.

The partially imidized PAA film with the negative patterns was transformed to the corresponding polyimide film with curing at 350 °C for 1 h. As shown in Figure 2b, the shape of the hemispheric structure on the etched film surface was maintained during the imidization. The negative image transformation from partially imidized PAA film to a polyimide film clearly shows that the precursor method is very useful for creating image patterns on some kind of thermoset polymer films. There have been a few reports about negative image film preparation using polysilane and polysiloxane films by ion beam irradiation.<sup>26–29</sup> Ours is the first case of obtaining a negative image in conventional and thermally stable polymer films.

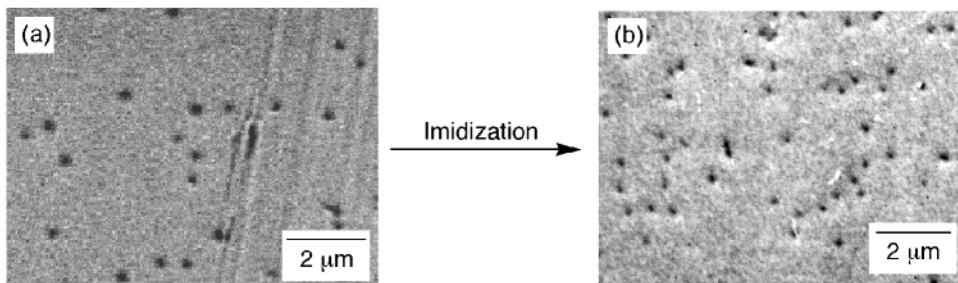
Figure 3a shows the SEM photograph of a film of PAA heated at 145 °C (84% polyimide content), followed by  $^{129}\text{Xe}^{23+}$  ion beam irradiation and etching in aqueous

(26) Seki, S.; Kanzaki, K.; Yoshida, Y.; Tagawa, S.; Shibata, H.; Asai, K.; Ishigure, K. *Jpn. J. Appl. Phys.* **1997**, *36*, 5361.

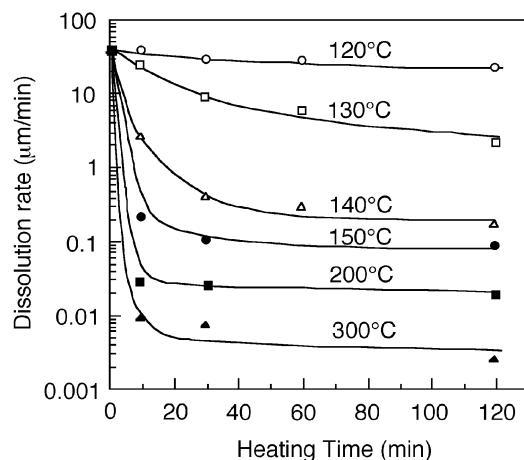
(27) Seki, S.; Shibata, H.; Yoshida, Y.; Ishigure, K.; Tagawa, S. *Radiat. Phys. Chem.* **1997**, *49*, 389.

(28) Seki, S.; Kanzaki, K.; Kunimi, Y.; Tagawa, S.; Yoshida, Y.; Kudoh, H.; Sugimoto, M.; Sasuga, T.; Seguchi, T.; Shibata, H. *Radiat. Phys. Chem.* **1997**, *50*, 423.

(29) Seki, S.; Maeda, K.; Kunimi, Y.; Tagawa, S.; Yoshida, Y.; Kudoh, H.; Sugimoto, M.; Morita, Y.; Seguchi, T.; Iwai, T.; Shibata, H.; Asai, K.; Ishigure, K. *J. Phys. Chem. B* **1999**, *103*, 3043.



**Figure 3.** SEM photographs of (a) the positive image on the PAA film heated at 145 °C (84% imidized PAA) followed by irradiating of  $^{129}\text{Xe}^{23+}$  ion beam and etching in aqueous 5% TMAH solution at 40 °C for 2 h and (b) the corresponding polyimide film with curing at 350 °C for 1 h.

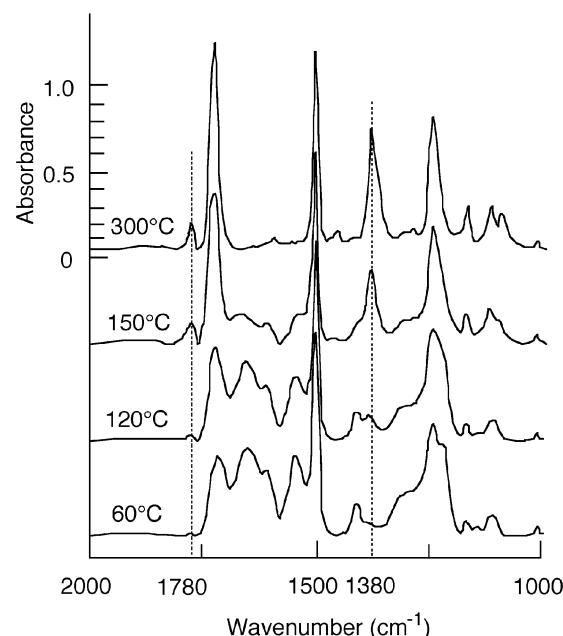


**Figure 4.** Dissolution rates of PAA films in aqueous 15% TMAH solution at 30 °C as a function of heating time of the films at 120 °C (○), 130 °C (□), 140 °C (△), 150 °C (●), 200 °C (■), and 300 °C (▲).

5% TMAH solution at 40 °C for 2 h. In contrast to the negative imaging of the 89% imidized film, a hole pattern with 0.3-μm pore diameter clearly appeared. The hole density was  $3.2 \times 10^7 \text{ cm}^{-2}$ , in good agreement with the accumulated ion fluence of  $3.0 \times 10^7 \text{ ions/cm}^2$ . This hole pattern formation indicates that the ion beam irradiation produced, in this case, positive imaging of the films, demonstrating how a slight drop of imidization temperature, that is, from 150 to 145 °C, reverses the imaging character of the films from negative to positive modes. Figure 3b shows the SEM photograph of the corresponding etched film fully cured to 100% imidization at 350 °C for 1 h, proving that a positive image can be transformed from a partially imidized PAA film to a polyimide film, as is the case with a negative image (Figure 2).

**Estimation of Imidization Degree Using ATR-IR.** The dependence of the ion beam imaging behavior on the imidization temperature of the PAA film shows that the imidization degree and the dissolution rate of the PAA film govern the mode of imaging. As imidization progresses, the dissolution rate of the film decreases, along with consumption of carboxyl groups. Therefore, reproducible control of the imidization degree of the precursor polymer is necessary for obtaining the desired ion beam imaging mode for partially imidized PAA films.

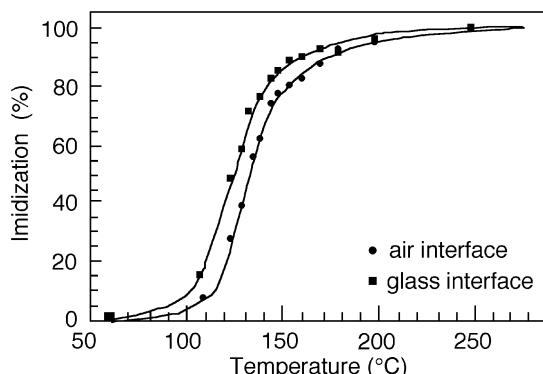
Figure 4 shows dissolution rates as a function of heating time of the films at 120, 130, 140, 150, 200, and 300 °C, respectively. The films were prebaked at 70 °C for 6 h in *vacuo* and at 100 °C for 2 h on a hot plate.



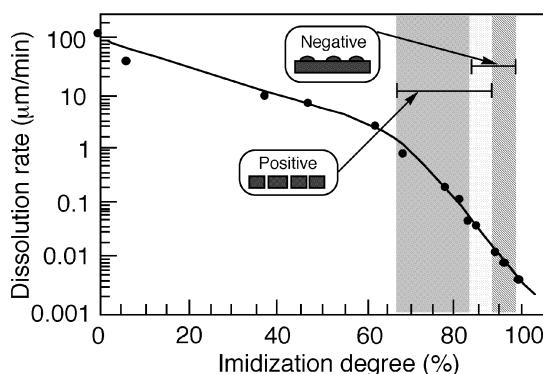
**Figure 5.** ATR-IR spectra of the PAA films heated at 60, 120, 150, and 300 °C for 1 h in a wavenumber region from 1000 to 2000  $\text{cm}^{-1}$ . Their spectra were recorded at the air interface of the films during the film preparation.

After heating, they were submerged in aqueous 15% TMAH solution at 30 °C. At each temperature, the dissolution rate of the film reached a constant value for heating times more than 1 h. Consequently, we fixed the heating time to 1 h for determining the imidization degree of partially imidized PAA films.

ATR-IR analysis was applied to determine the imidization degree for precursor polymer films because these films are too thick to be subjected to a conventional FT-IR analysis due to their strong IR absorbance. Figure 5 shows the ATR-IR spectra of the precursor films heated at 120, 150, and 300 °C for 1 h in a wavenumber region from 1000 to 2000  $\text{cm}^{-1}$ . These spectra were recorded at the air interface of the films, that is, the exposed surface during the film preparation. The peak intensity at 1380  $\text{cm}^{-1}$ , assigned to absorbance of the imide ring (C=N), gradually increases as the imidization temperature is raised from 60 to 300 °C; furthermore, the peak intensity at 1380  $\text{cm}^{-1}$  is quite strong (absorbance; 0.6) in the 100% imidized film. Therefore, the imidization degree of the partially imidized films is calculated based on the intensity at 1380  $\text{cm}^{-1}$  compared to the standard peak at 1500  $\text{cm}^{-1}$ , assigned to the aromatic rings. The calculation was undertaken on the assumption that PAA films heated



**Figure 6.** Imidization degrees of the PAA at (●) the air and (■) glass interfaces during the film preparation, as a function of imidization temperatures. The imidization degrees were calculated on the basis of peak absorbance at  $1380\text{ cm}^{-1}$  in ATR-IR spectra.



**Figure 7.** Plots of the dissolution rates of the partially imidized PAA films in aqueous 5% TMAH solution at  $40\text{ }^\circ\text{C}$  as a function of the imidization degrees along with the ion beam imaging modes (positive and negative).

at  $60$  and  $300\text{ }^\circ\text{C}$  are composed of  $0$  and  $100\%$  imidized PAA, respectively.

Figure 6 shows the degree of imidization of PAA at the air and glass interfaces, calculated on the basis of peak absorbance at  $1380\text{ cm}^{-1}$ , as a function of imidization temperature. The degree of imidization increases drastically in the temperature range of  $120$ – $170\text{ }^\circ\text{C}$  and then increases moderately from  $170$  to  $250\text{ }^\circ\text{C}$ ; above  $250\text{ }^\circ\text{C}$  the rate of increase begins to taper off. The imidization of the partially imidized PAA films at the air interface were  $10$ – $20\%$  lower than those at the glass interface, probably because the temperature of the films near the glass interface proximate to the heat source was higher than that near the air interface during imidization. Accordingly, we defined the imidization degree of PAA of each film as the average of the imidization degrees at the air and glass interfaces.<sup>30</sup>

**Imaging Mode of the Films Controlled by Imidization Degree of PAA.** In Figure 7, the dissolution rates of the partially imidized PAA films in aqueous 5% TMAH solution at  $40\text{ }^\circ\text{C}$  were plotted as a function of imidization along with the ion beam imaging modes, positive or negative, as observed by SEM photographs. The plot of the imidization of PAA is classified into three regions: (1) a positive image region from  $67$  to  $83\%$ , (2) a boundary region of negative and positive images from

$84$  to  $89\%$ , and (3) a negative image region from  $89$  to  $94\%$ . These positive and negative images appeared in the range ( $67$ – $94\%$ ) where the dissolution rates of the partially imidized PAA film changed drastically with changes in imidization. Accordingly, the imaging mode of the film changed from negative (Figure 2) to positive (Figure 3) with very slight changes in the imidization temperatures, corresponding to the narrow imidization range of the boundary region ( $84$ – $89\%$ ).

There have been many reports on the mechanism of ion beam positive imaging in PET and PC, wherein a scission of the polymer main chains takes place by ion beam radiation, resulting in the decrease of the molecular weight of the polymers.<sup>31–33</sup> Accordingly, the positive images in the films with the imidization degrees of PAA ranging from  $67$  to  $89\%$  should be due to the scission of the polymer main chains. On the other hand, it is not easy to elucidate why the slight difference of imidization degree causes the reversal of image mode for the partially imidized PAA films. Only a few reports related to negative imaging of polymer films by ion beam radiation are known. The sole explanation given for this phenomenon has been cross-linking resulting from the energy deposition of the ion beams in polysilane and polysilicone films.<sup>26–29</sup> We tested for two other possibilities. Since the carboxyl groups in PAA must play an important role for the imaging mode owing to their affinity with alkaline solutions, we postulated that irradiation-induced imidization and decarboxylation of the PAA might have decreased the dissolution rate of the irradiated films in the alkaline etchant.<sup>33</sup> The change in the chemical structure of  $89\%$  imidized PAA films by  $^{129}\text{Xe}^{23+}$  ion beam irradiation with accumulated fluence of  $1.0 \times 10^{10}\text{ ion/cm}^2$  was evaluated using ATR-IR. Subtraction spectra of the  $89\%$  imidized PAA films before and after the irradiation showed almost no change in the region of carbonyl groups from  $1500$  to  $1800\text{ cm}^{-1}$ , even though the fluence of the  $^{129}\text{Xe}^{23+}$  ion was higher by 3 orders than that for the negative imaging. Accordingly, we ruled out decarboxylation by ion beam irradiation as the mechanism for negative imaging. Another possible reason for the change in the dissolution rate of the film by irradiation is morphological alteration. X-ray diffraction spectra of the  $89\%$  imidized PAA film before and after the irradiation indicate no appreciable morphological alteration. From these spectral results, we propose that the imaging mode is altered by a slight change in the balance of scission and cross-linking in the polymer main chains with degree of imidization. Both of these reactions are responses to energy deposition from the ion beam.

## Conclusions

Dual-tone imaging of polyimide films was achieved by  $^{129}\text{Xe}^{23+}$  ion beam irradiation of the partially imidized PAA films, followed by alkaline etching in aqueous TMAH solution and heat curing of the imaged films. In

(31) Stecknreiter, T.; Balanzat, E.; Fuess, H.; Trautmann, C. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1999**, *151*, 161.

(32) Steckenreiter, T.; Balanzat, E.; Fuess, H.; Trautmann, C. *J. Polym. Sci. Polym. Chem.* **1999**, *37*, 4318.

(33) Friese, K.; Placek, V.; Mehnert, R.; Angert, N.; Spohr, R.; Trautmann, C. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1995**, *105*, 139.

partially imidized PAA film with imidization ranging from 89 to 94%, ion beam irradiation produced a hemispheric tracked structure with  $1.0\text{-}\mu\text{m}$  height and  $1.5\text{-}\mu\text{m}$  diameter. In contrast, a positive hole pattern with  $0.3\text{-}\mu\text{m}$  diameter appeared on the precursor polymer films with imidization ranging from 67 to 83%.

Positive and negative images were considered to be switched by a slight change in the balance of scission and cross-linking of the polymer chains, resulting from energy deposition of the ion beam.

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