Surface Relief and Porous Structure Patterning of Polyimide

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Polyimides have excellent properties such as thermal stability, mechanical strength, and chemical stability, which are widely used as the materials for microelectronics and aerospace. We discover the new process of porous structure patterning and surface relief patterning. Porous structure patterning of polyimide is based on poly (amide acid) and photo acid generator (PAG, NA100). Photo irradiation of the PAA in the presence of PAG induce surface relief grating after thermal imidization. The tone can be controlled using PAG or PBG. The mechanism of the pattern formation is based on the change in imidization temperature by the PAG or PBG.

Keywords: polyimide, photo acid generator, photo base generator, porous structure patterning

1. Introduction

The chemical and physical characteristics of polyimide (PI) are indispensable for numinous application to semiconductor, display and aerospace industry. In addition, polyimide with functionalization such as photosensitivity [1-11], photoconductivity [12-15], transparency [16-20], and so on are developed by designing their structure [21-27]. This kind of research is widely held and verity of photosensitive polyimide was invented.

In this study, we report a new patterning system of chemical amplified negative-type PI based on a poly amide acid (PAA(PMDA/ODA)) and photo acid generator (PAG, NA100), positive-type PI based on PAA and photo base generator (PBG, NBC105) without development process and porous structure patterning PI using chemical imidization.

PAG or PBG were decomposed by photo irradiation, generates acid or base respectively and the generated acid or base will act as a catalyst for the low temperature imidization. The formation of this PI is simple, just the addition of PAG or PBG to PAA solution in NMP. This solution is bar-coated and baked. Then, the film is exposed the light of Xe lamp to produce acid or base. Upon thermal treatment of this film, acid or base catalyzes the imidization. The deference of imidization late between exposed and unexposed area lead the surface relief image.

Furthermore PAA film containing PAG gets porous structure patterning on exposed area by chemical imidization after photo irradiation.

2. Experimental

2.1 Materials

Pyromellitic anhydride (PMDA) purchased from Wako chemicals was recrystallized from acetic anhydride and drying under reduced pressure at 170 ºC for 2 h before use. 4, 4'-Oxydianiline (ODA) purchased from Wako Chemicals was recrystallized from ethanol. N-methylpyrrolidone (NMP) purchased from

Received May 17, 2010
Accepted June 11, 2010
Wako chemicals was dried over molecular sieves (4A). Acetic anhydride and pyridine was dried over molecular sieves (3A). NAI-100 used as a PAG and NBC-105 used as a PBG were supplied by Midori Kagaku.

2.2 Synthesis of PAA (PMDA / ODA)

PMDA (12.53 g, 51.4 mmol) was added to a solution of ODA (11.5 g, 51.4 mmol) in NMP (220ml). The mixture was stirred at 0 °C, and then warmed up to room temperature for 24 h to give viscous clear solution with quantitative yield. The concentration of PAA was adjusted to 15 wt%.

2.3 Porous structure patterning

Photosensitive polymer films were prepared by bar-coating on grass plates from 15 wt% PAA solution in NMP containing 10 wt% PAG, followed by prebaking at 70 °C for 30 min. The films were exposed to light with a Xe lamp without using optical filters. They were subjected to post exposure bake (PEB) at 110 °C for 1 min. Chemical imidization of the exposed films was carried out by heating at 40 °C for 30 sec in mixed solution of acetic anhydride and pyridine.

2.4 Surface relief patterning

Photosensitive polyimide films of 15 wt% solid content in NMP solution containing 10 wt% PAG or 10 wt% PBG were bar-coated on grass plates, followed by prebaking at 70 °C for 30 min. They were exposed with a Xe lamp without using any optical filters. The sample films were gradually baked at 120, 160, 200, 240 °C respectively for 20 min.

2.5 Degree of imidization

Sample films with thickness of about 1 μm were heated from 70 °C to 300 °C for 20 min. The film heated up to 300 °C was used as the reference film with imidization degree of 100 %. Absorption on FTIR spectra at 1770 cm⁻¹ and 1500 cm⁻¹ was measured, and imidization ratio was determined as,

\[ A = \frac{I_{1770}}{I_{1500}} \]

\[ r_1 = \frac{(A_rA_{55})/(A_{300}A_{55})}{I_{1770}} \times 100 \]

where \( A_1 \) and \( I_1 \) are intensity ratio and IR signal intensity at the temperature \( T \), respectively.

3. Results and Discussion

3.1 Porous structure patterning

The optical microscope images in Fig.1 show the porous structure prepared by the exposure, the following thermal treatment and chemical imidization of PAA (PMDA/ODA) containing 10 wt% PAG. The dark area stands for cloudy part and the light area stands for transparent part. Zooming up the dark area in Fig.1 (a), many homogeneous holes are observed whose diameter is almost 5 μm. Fig.2 shows the SEM image of the photo irradiated part of the PI film. Showing in Fig.1, The holes are separated globular shape, whose diameter is almost 4 μm.

![Microscope images of porous structure patterned on PI with PAG (10 wt%) after photo-irradiation of 30 min followed by thermal treatment at 110 °C for 1 min and chemical imidization](image-url)
The microscopic image in Fig.3 shows porous structure of PI containing 10 wt% methane sulfonic acid in PAA. This reveals acid effect the preparation of porous structure. Many pores are observed similar with the PAA film containing PAG, showing that the pore generation is due to the existence of an acid rather PAG itself.

Fig.4 shows the correlation between acid amount and transmission of the sample film containing 10 wt% PAG, exposed by a Xe lamp for 5, 10, 20, 30, 60 min followed by chemical imidization. As irradiation time increases, transmission of the PI film decreases due to the porous structure generation which is catalyzed by the acid. Thus the porous structure formation is confirmed as the influence of acid generation of PI.
To investigate the mechanism of the negative tone relief patterning, degree of imidization during thermal treatment was measured with FTIR spectroscopy. Fig.6 shows the change in imidization. The PAA containing acid is converted to PI at the lower temperature compared to the PAA without an acid. As can be seen from this result, acid generated from PAG works as the catalyst of low temperature imidization. Thus the exposed area of the PAA containing 10 wt% PAG is subjected to thermal imidization below 150 °C, while imidization of the unexposed area occurs about 170 °C, or the Tg of the PAA.

Fig.6 The degree of imidization of PAA (PMDA/ODA) with or without methane sulfonic acid. PAA containing 10 wt% methane sulfonic acid (●) PAA without acid (○).

Fig.7 shows the relationship between the depth of pattern and the annealing history of PAA (PMDA/ODA) containing 10 wt% PAG films, which were prebaked at 70 °C for 30 min and exposed for 30 min through a photo mask, and then they were heated at each temperature (100, 120, 140, 160, 180, 200, 240 °C) for 10 min. Relief contrast is maximum when heated up to 150 °C, when the mobility of polymer chain becomes largest because the Tg is about 170 °C. The PAA in unexposed area should be remains as PAA, while the PAA in exposed area should be converted from PAA to PI. Above the Tg relaxation of PI chain should decrease the surface relief.

3.3 Surface relief patterning containing PBG

Fig.8 shows the profile of surface relief patterning of polyimide made from PAA containing PBG after exposure and the thermal imidization.

Fig.8 Surface relief profile of PAA containing PBG (10 wt%) after photo irradiation of 30 min by Xe lamp without filter followed by thermal treatment

The profile of the PAA containing PBG is, however, positive which is quite contrast to the case of PAA with PAG. Fig.9 shows change in the imidization degree of the PAA containing imidazole during thermal imidization. PAA's including a base are converted to PI at lower temperature compared to the PAA without base. Base generated from PBG works as a catalyst of low temperature imidization.

Fig.7 The relation between depth of pattern and annealing history of PI (PMDA/ODA) containing PAG (10 wt%) after photo irradiation of 30 min by a Xe lamp without filter followed by thermal treatment for 10 min at each temperature.
Fig. 9 Degree of imidization of PAA (PMDA/ODA) with or without imidazole
PAA containing 10 wt% imidazole (●) PAA without imidazole (○)

Fig. 10 shows the relationship between the depth of pattern and the annealing history. The PAA containing 10 wt% PBG films were prebaked at 70 °C for 30 min and exposed for 30 min through a photo mask. Then they were heated at each temperature (100, 120, 140, 160, 180, 200, 240 °C) for 10 min, and the depth of pattern was measured.

The depth of photo-irradiated part increases as the PAA is converted to PI catalyzed by the base from PBG below 150 °C. The depth decreases due to the spontaneous imidization of unirradiated part above 150 °C. Magnitude of the shrinkage of the unirradiated should be large than that of photo-irradiated part become the molecular packing is large when imidization is performed at the high temperature due to larger molecular relaxation. Thus the negative tone pattern formation of PAA/PBG is based on the difference in the imidization temperature between photo-irradiated and unirradiated parts. This mechanism is common to positive tone pattern formation of PAA/PAG system. The acids generated from PAG also catalyze depolymerization of PAA, which is the reason for the larger depth in the photo-irradiated part in PAA/PAG system.

4. Conclusions

Porous structure patterning of PAA containing PAG was performed by chemical imidization. Pores are observed in the exposed area. Porous generation is induced by acid. PAA containing PAG generates negative tone surface relief upon photo irradiation, while that containing PBG generates positive tone, which is explained by the imidization temperature and depolymerization.

Reference
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