Photo-induced Surface Modification of Polyimides for Printable Electronics Fabrication

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ABSTRACT

Manufacturing flexible electronic devices with printing technique is one of the key steps, but printing fine structure with ink jet technique is relatively limited, because positional precision of ink droplet deposition and the size of an ink droplet are not smaller than several microns.

We prepared those polyimides whose surface wetability can be changed by photoirradiation, with which surface wetability can be photo-lithographically patterned to make channels and an ink droplet spread along the patterned area with photolithographic resolution. The degree of surface contact angle change of water on the polyimide is as large as 70° between before and after the photoirradiation. The mechanism is confirmed as the chemically amplified reaction of t-BOC group, and photochemical reaction of benzophenone moiety.

Surface relief structure can be also patterned only by exposure without development with those polyimides containing PAG or PBG as additives. The mechanism is determined as the difference in the imidization temperature. Positive or negative tone of the relief can be controlled by the selection of the additives. Porous structure pattering with turbid/transparent structure can be also patterned by photoirradiation. Those polyimides are potentially high performance and functional materials for printable and flexible electronic devices.

Keywords: polyimide, surface relief, wetability, patterning

1 INTRODUCTION

Polyimides are one of the thermostable polymers with mechanical strength, size precision throughout temperature change, which are one of the reliable substrates used for printable and flexible electronic devices.

Manufacturing devices with printing technique is one of the key steps in developing printable and flexible electronics or photonics technology. Printing fine structures with ink jet technique is relatively limited, however, because positional precision and size of an ink droplet are not smaller than several microns. One of the innovational solution for those problems is the combination of photolithography with fine resolution and ink jet technique with on demand and convenience, where surface wetability contrast is photolithographically patterned on the substrate with high precision, and then ink droplets should spread along the patterned area during ink jet process [1].

We prepared those polyimides whose surface wetability can be changed by photoirradiation, with which surface stability can be photo-lithographically patterned to make channels and ink droplets spread along the patterned area with photolithographic resolution.

Expanding this technique made it possible to perform surface relief pattering or porous structure patterning on the surface polyimide only by exposure without development.

Combination of those techniques may be one of the innovating process and materials for the fabrication of printable and flexible electronic devices.

2 EXPERIMENTAL

2.1 Materials

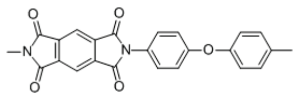
Pyromellitic dianhydride (PMDA) purchased from wako was recrystalized from acetic acid dianhydride and dried under reduced pressure at 170°C for 2h before use. 4,4'-Oxydianiline (ODA) purchased from wako was recrystalized from ethanol. *N*-Methylpyrrolidinone (NMP) purchased from wako was dehydrated over molecular sieves 4A. NAI-100 as a PAG and NBC-105 as a PBG were supplied by Midori Kagaku, which were used without further purification. Structure of the materials and polyimides are shown in Figure 1.

2.2 Preparation of Polyimde Precursors

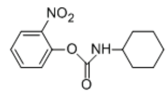
PMDA (12.53g, 51.4mmol) was stepwisely added to a solution of ODA (11.5g, 51,4mmol) in NMP (220ml), and then the mixture was stirred at 0°C for 30 min, followed by the mixing at room temperature for 24h to give a viscous clear solution. Other poly(amide acid) solutions were similarly prepared.

2.3 Preparation of tBoc-Protected Polyimde

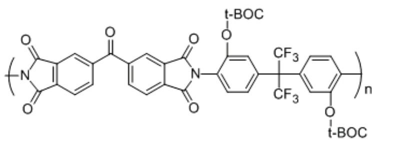
BTDA (2g, 6.20 mmol) and 6FAP(2.27g, 6.20 mmol) were solved in 12ml of NMP under ice cooling, which was stirred at room for 20 hours to give PAA(BTDA/6FAP). The PAA was imidized by warming to 60°C in the presence of pyridine (100 ml) and acetic anhydride (100 ml) to give soluble PI. The PI(BTDA/6FAP) (0.2g) was solved in chloroform (30 ml) and then di(t-butyl) carbonate (0.401g, 1.83 mmol) was added and refluxed for 3 hours to give tBoc-PI(BTDA/6FAP).



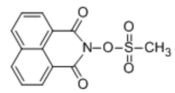
PI(PMDA/ODA)



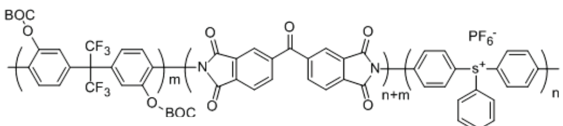
NBC-105



tBOC-PI(BTDA/6FAP)



NAI-100



tBOC-PI(BTDA/6FAP/SSDA)

Figure 1: Chemical Structure of polyimides (PI) , a photo acid generator (PAG) and a photo base generator.

2.4 Preparation of Polyimde Containing Photo Acid Generating Unit, PI(BTDA/6FAD/SAD)

6FAD (3.296g, 0.9 mmol) and SDA (0.216g, 0.1 mol) were solved in NMP (30 ml), which was stepwisely added with BTDA (3.222g, 1 mmol) to give a polyamide acid PAA(BTDA/6FAD/SDA). The PAA was chemically imidized by heating at 60°C in pyridine/acetic anhydride mixed solution for 5 hours. to give corresponding PI. The PI (1.2g) was heated up to 130°C for 4 hours in the presence of diphenyliodonium hexafluorophosphate (0.432g ,1.01 mmol) and cupric benzoate (5 mg, 0.01 mmol). The product was treated by di(t-butyl)carbonate (0.74g, 3.39 mmol) in the presence of dimethylamino-pyridine (5mg, 0.04 mmol) at 70°C for 3 hours. to give tBOC-PI(BTDA/ 6FAD/SSDA).

2.5 Photolithographic Pattering Condition

A photosensitive polymer film was prepared by bar coating of 15 wt% polymer solution in NMP onto a glass plate. The film was prebaked at 70°C for 30min. Photoirradiation was performed with a Xe lamp, and then the film was post exposure baked (PEB) at 110° for 1 min.

2.6 Determination of degree of imidization

FTIR was measured for the sample polymer films with thickness of 1μm. Relative ratio of the absorption at $1770 cm^{-1}$ and $1500 cm^{-1}$ was calculated and normalized with the data of the sample film heated up to 300°C as the standard of fully imidized one.

3 RESULTS AND DISCUSSION

3.1 Surface Relief Patterning of Polyimides without Development.

Figure 2 shows the surface relief pattern on a polyimide film, PI(PMDA/ODA), which is obtained by exposure to the substrate film of PAA(PMAD/ODA) containing 5% PBG (NBC-105), followed by thermal treatment up to 250°C for 30 min. The film is apparently transparent with surface relief pattern of negative tone corresponding to the photomask pattern. The depth of the relief profile of longitudinal cross section of the PI(PMDA/ODA) is as ca.0.3 μm in depth.

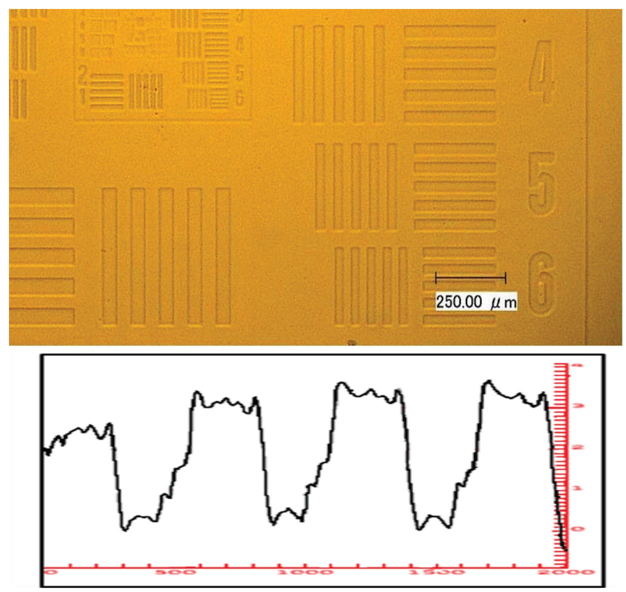


Figure 2: Surface relief pattern of PI(PMDA/ODA) containing 5% NBC-105 after exposure and thermal treatment up to 250°C without development (upper picture). Relief profile of longitudinal cross section of the patterned film surface (lower picture).

Positive tone pattern has been obtained after the exposure and thermal treatment of the PAA sample film with addition of a PAG (NAI-100) instead of the PBG. In order to clarify the mechanism of the surface relief formation, temperature dependence of imidization degree was measured in the presence of an amine (Figure 3). Imidization of a PAA(PMADA/ ODA) usually completed around 175°C, which is the glass transition temperature, *Tg*, of the PAA where molecular motion for imidization is relaxed. On the other hand, the imidization of PAA occurs at 120°C in the presence of an amine, showing that the *Tg* of polymer-amine complex decreases to induce low-temperature-imidization. Similar phenomenon is observed for the imidization of PAA in the presence of an acid, where an acid catalyzed imidization reaction by the protonation and activation of the carbonyl group.

Change in the pattern height of PAA containing PBG sample during thermal treatment after photoirradiation is shown in Figure 4. The height of irradiated area decreases relative to the unirradiated area during the thermal annealing up to 150ºC. Then the depth of the depression decreases and it becomes higher than the unirradiated area above 200ºC to generate negative tone pattern. Based on the observation, the mechanism of negative tone pattern formation of PAA/PBG system is explained as follows. imidization temperature of the photoirradiated area decreases to 120 ºC due to the generation of a base, while that of the unirradiated area remains to 175 ºC. Then thermal imidization of the irradiated area occurs preferentially during the thermal annealing up to 120 ºC to make depressive pattern due to shrinkage by imidization, then the unirradiated area begins to shrink due to imidization above 170 ºC.

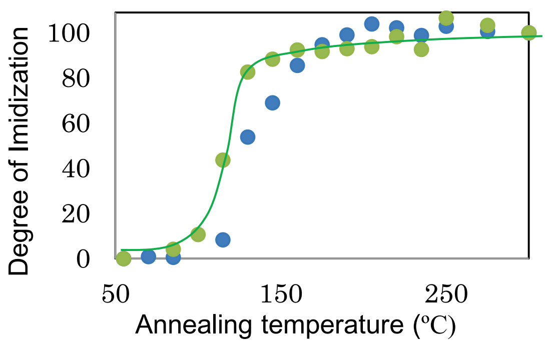


Figure 3: Degree of imidization during thermal annealing of PAA(PMDA/ODA) containing 10% imidazole (green line) and without additives (blue dots).

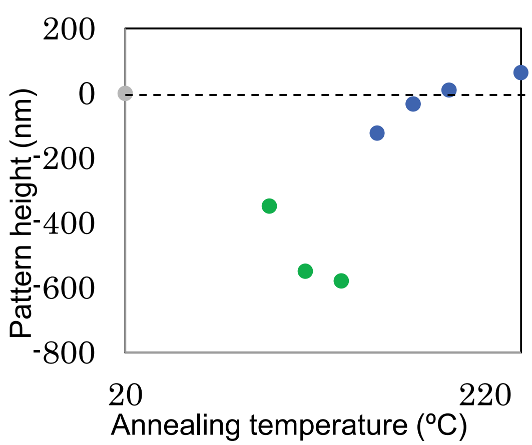


Figure 4: Change in the pattern height of PAA(PMDA/ ODA) containing 10% imidazole during thermal treatment after photoirradiation.

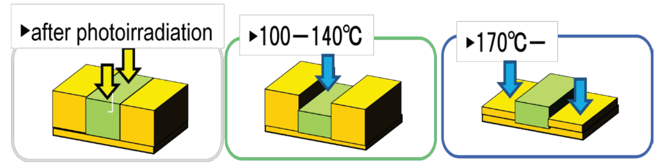


Figure 5: Illustration of negative pattern formation of PAA containing PBG during thermal treatment. Center part of substrate (green area) is photoirradiated, which initially depresses due to the shrinkage of low-temperature-imidization. The unirradiated area (yellow) depresses much more due to high-temperature imidization.

Density of the low-temperature-imidization area is small because molecular mobility is limited and the packing of polymer chain becomes poor. On the other hand, the high-temperature-imidization area is well molecular-packed due to molecular mobility is relaxed. Thus the tone reverses to make negative tone surface relief pattern (Figure 5).

Thus, positive or negative tone can be controlled by the selection of the additives, PAG or PBG, with our technique, which eliminates development process to open a new way to manufacturing devices.

3.2 Porous Structure Patterning of Polyimide

PAA(PMDA/ODA) containing 10 wt% PAG was photoirradiated similarly with the experiments described above section, but the sample film was subjected to chemical imidization by immersing in acetic anhydride/ pyridine mixed solution before thermal imidization. Figure 6 shows the optical microscope image of the film, in which the photoirradiated area is turbid and unirradiated area remains transparent. The right picture of Figure 6 shows that small bubbles are generated in the photoirradiated area. Figure 7 shows the SEM image of the pores of the PI, whose size is 5μm and quite homogeneous in distribution.

The pore formation depends on the chemical imidization conditions. Namely, the pores are generated when the chemical imidization is performed up to 40ºC, while the film becomes transparent subjecting chemical imidization above 70ºC, meaning that the segregation of

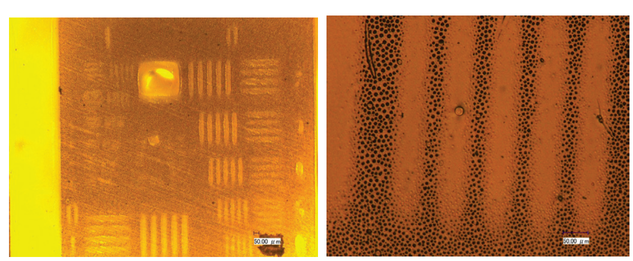


Figure6: Porous structure patterned picture of PAA(PMDA/ ODA) containing 10% PAG after photoirradiation, chemical imidization, and thermal annealing (left). Magnification of the patterned area of left picture with small bubbles (right).

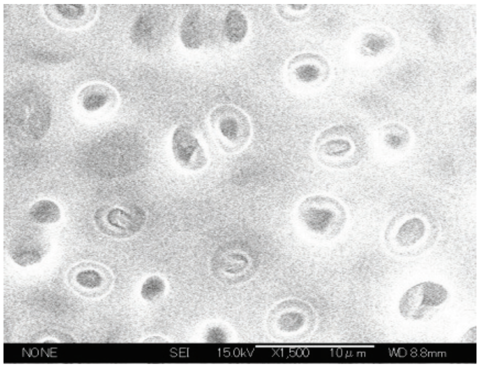


Figure 7: SEM image of the porous area of PI(PMDA/ODA) containing 10% PAG after photoirradiation and chemical imidization at 40ºC. Size of the bubbles is 5μm and quite homogeneous in distribution.

polymer chain during chemical imidization process affect on the pore formation.

3.3 Surface Wetability Patterning of Polyimides

Change in the surface contact angle of water droplet on a tBoc-protected polyimide, tBOC-PI(BTDA/6FAP), containing a PAG, NAI-100, by photoirradiation was investigated using photoinduced structural change, which can be applied as the hydrophilic/ hydrophobic contrast patterning technique in printable and flexible electronics. Figure 8 shows the contact angle change of tBOC-PI(BTDA/6FAP) before and after the photoirradiation. The contact angle changes from 61.5º to 18.3º, showing wetablity of the film surface increase upon the photoirradiation. The mechanism involves photoinduced acid generation of NAI-100 and the following acid catalyzed deprotection of tBOC group to convert polar hydroxy group.

Figure 8: Surface contact gale of water droplet on tBOC-PI(BTDA/6FAP) before and after photoirradiation.

We prepared tBOC-PI(BTDA/6FAP/SSDA) in order to incorporate the PAG and tBOC unit into the on polymer chain to increase the photoreactivity. Figure 9 shows the change in the surface contact angle of water droplet on tBOC-PI(BTDA/6FAP/SSDA) during the photoirradiation. The wetability increases as the increase in photoirradiation time, and the magnitude to the change is as high as 70º.

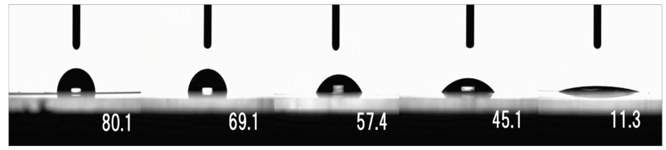


Figure 9: Surface contact angle of water droplet on tBOC-PI(BTDA/6FAP/SSDA) during the photoirradiation of 0,15, 30, 45,60 min respectively.

Measuring XPS of tBOC-PI(BTDA/6FAP/SSDA), binding energies of 168 and 164 eV are observed for S atoms before photoirradiation, which change to 169 eV, showing the disappearance of sulfonium salts. Double peaks around 401 eV of N atoms changes single peak, showing that the nitrogen atoms of imide moiety becomes homogeneous due to the decomposition of sulfonium salts. Appearance of small shoulders above 265 eV of carbonyl carbons shows that hydroxy group generation by the excitation of benzophenone carbonyl group [3], which also contributes to the increase in the wetability.

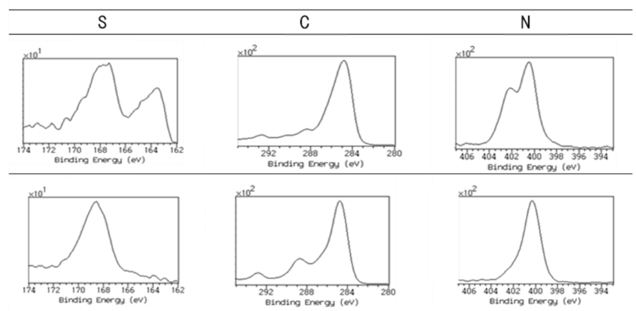


Figure 10: XPS spectra of tBOC-PI(BTDA/6FAP/SSDA) before photoirradiation (upper spectra), and after photo-irradiation (lower spectra).

4 CONCLUSION

Sufficient large change in surface wetability can be induced by the photoirradiation of polyimide derivatives. Surface relief pattern or porous pattern can be also induced easily by the photoirradiation. Those technique and materials may be potentially innovative for printable and flexible electronics device fabrication.

REFERENCES

[1] Y. Tsuda, "Polyimides Bearing Long-Chain Alkyl Groups and Their Application for Liquid Crystal Alignment Layer and Printed Electronics" in INTECH Book, "Liquid Crystal Displays" ISBN 978-953-307-899-1, (2011).

[2] F. Kodera, Y, Matsuzawa, K. Okano, E. Tomiyama, T. Yamashita, *J. Photopolym. Sci. Tech.,* **23**, 235-240 (2010).

[3] Higuchi, T. Yamashita, K. Horie, and I. Mita, *Chem. Mater*. **3**, 188-194 (1991)