Development of Photosensitive Imide-containing Vinyl Polymers Based on Reaction Development Patterning

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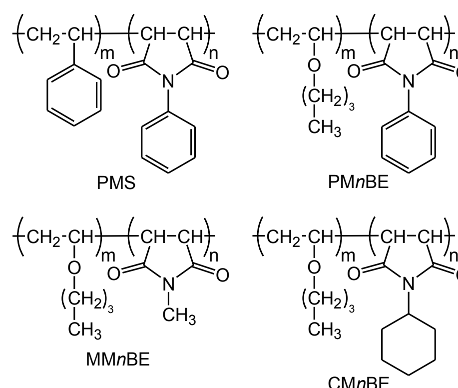
Introduction

Photosensitive polymers are materials for fine pattern formation, which utilize the difference of solubility between exposed and unexposed areas caused from UV irradiation. They are indispensable in electronic industry such as the field of manufacturing of integrated circuits (ICs), buffer-coat layers for IC chips, interlayer dielectric films and printing plates [1]. In the application of buffer coats and interlayer dielectrics, the polymers are required to have high thermal, mechanical and electrical properties. Therefore, photosensitive polyimides are widely utilized to satisfy the requirements [2]. They are mainly composed of poly(amic acid) derivatives and post-curing at high temperature (~ 300 °C) is indispensable for conversion of amic acids to imide groups.

In contrast, we have developed a novel pattern-forming method, reaction development patterning (RDP) [3]. By use of mixture of a polymer with carboxylic-acid-derivative linkages (such as imides in the main chain) and a photosensitive agent (such as diazonaphthoquinone (DNQ)), RDP can afford fine patterns by photo-irradiation to a film composed of polymer / photosensitive agent and the following development with a solution containing nucleophiles. The key reaction of RDP is main-chain scission by nucleophilic acyl substitution between -C(O)-X- bonds in a polymer and nucleophiles in a developer. RDP can also give photosensitivity to vinyl polymers having imide groups in their side chain by utilizing change in solubility induced by reaction of imides with nucleophiles in a developer to afford amic acids [4]. However, the pattern formation has been achieved only when alkoxide was used as a nucleophile in developer, though alkoxide is water-unstable and hard to deal with it.

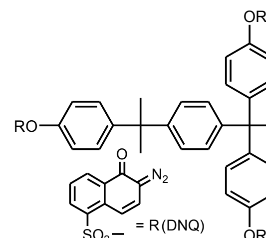
In this study, we reported pattern formation of photosensitive imide-containing vinyl polymers by application of RDP with OH^- of tetramethylammonium hydroxide (TMAH) as a nucleophile in developer. We used copolymers of PMS, PM*n*BE, MM*n*BE and CM*n*BE as vinyl polymers (Scheme 1).



Scheme 1 Structures of imide-containing vinyl polymers

Results and Discussion

Imide-containing vinyl polymers were synthesized by radical copolymerization of maleimides with electron-donating monomers [5, 6]. Pattern formation from PM*n*BE is shown as an example of RDP. 20 wt% of PM*n*BE was dissolved in *N*-methylpyrrolidone (NMP). BADNQ3 (Scheme 2) as a photosensitive agent (20 wt% for PM*n*BE) was dissolved in the NMP solution. The resulting photosensitive PM*n*BE solution was degassed and spin-coated onto a mat side of a copper foil, and prebaked at 90 °C for 10 min in a far-infrared oven. The obtained film was then irradiated by an ultra high-pressure mercury lamp without any filter at both i and g lines through a photomask with a contact technique. The exposed film was developed with a TMAH / H_2O / NMP / MeOH solution (2 / 5 / 5 / 18 (weight ratio)) at 50 °C under ultrasonication, and rinsed with H_2O. As a result, positive-tone patterns of PM*n*BE was obtained as shown in Fig. 1a. Table 1 shows the results of RDP-based pattern formation from various imide-containing vinyl polymers. Comparing the effects of side-chain functional groups on development properties, it was clarified that use of *n*-butyl vinyl ether in place of styrene as a comonomer of maleimide highly improved solubility of the exposed areas and ability of pattern formation (entries 1-3). This would be because the presence of relatively hydrophilic and flexible alkyl ether chain promotes permeation of the developer. PM*n*BE gave patterns of higher residual thickness with shorter



Scheme 2 Photosensitive agent, BADNQ3

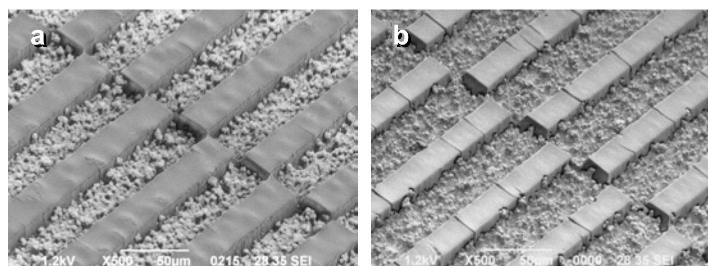


Fig. 1 SEM images of photosensitive vinyl polymers based on RDP, a) PM*n*BE (Table 1, entry 2), b) MM*n*BE (Table 1, entry

development time than MM*n*BE (entries 2, 3). This would be due to higher reactivity of imide carbonyls in PM*n*BE than those in MM*n*BE, which comes from more extended delocalization of a lone pair on imide nitrogen, not only with carbonyl groups but with phenyl group, in PM*n*BE. On the other hand, dissolution rate of CM*n*BE is much slower than PM*n*BE and MM*n*BE and little difference in residual thickness was observed even after one-hour development (entry 4). Hydrophobic and non-conjugated cyclohexyl group in CM*n*BE would inhibit permeation of the hydrophilic developer into the film and reduce reactivity of imide groups. SEM images of the patterns from PM*n*BE and MM*n*BE are shown in Fig. 1.

Table 1 Results of pattern formation of photosensitive imide-containing vinyl polymers based on RDP[1,2)]

Entry	Polymer	Development time [min'sec]	Film thickness[3)] [μm]		Dissolution rate [nm/s]		Residual thickness [-]		Resolution[5)] [μm]
			Exposed	Unexposed	Exposed	Unexposed	Exposed	Unexposed	
1	PMS	59'59	10.4 → 0.3	10.4 → 0.4	2.8	2.8	(0.03)[4)]	(0.04)[4)]	-[6)]
2	PM*n*BE	1'37	8.5 → 0	8.5 → 7.2	88	13	0.00	0.85	10
3	MM*n*BE	4'51	9.3 → 0	9.3 → 6.8	32	8.6	0.00	0.73	20
4	CM*n*BE	59'59	7.3 → 6.7	7.3 → 6.7	0.17	0.17	(0.92)[4)]	(0.92)[4)]	-[6)]

1) Additive: BADNQ3 (20wt% for polymer), Solvent: NMP, Pre-baking: 90°C/10min, Exposure dose: 300mJ/cm^2
2) Developer: TMAH/H_2O/NMP/MeOH = 2/5/5/18 (weight ratio), Development: 50°C/ultrasonication
3) By contact type thicknessmeter 4) No clear difference between exposed and unexposed area 5) By SEM 6) No fine pattern

Sensitivity curve of PM*n*BE with BADNQ3 system is shown in Fig. 2, and sensitivity (D_0) where the film thickness became zero was 401 mJ/cm^2.

To elucidate the mechanism of the pattern formation, we carried out model reaction using PM*n*BE. PM*n*BE was reacted with TMAH / H_2O / NMP / MeOH (2 / 5 / 5 / 18 (weight ratio)) mixture in a flask at [C=O in PM*n*BE] / [TMAH] = 1 / 2 (molar ratio) for 1 h at r.t., and IR spectra of PM*n*BE and the product isolated after neutralization were shown in Fig. 3. In the IR spectrum of the product, C=O and C-N stretching absorptions derived from imide group were decreased, and N-H and C=O absorptions derived from amide and carboxyl groups appeared. These results indicate that imide rings in PM*n*BE was opened by the nucleophilic reaction with OH^- in TMAH as a nucleophile. The reaction product became soluble in developer though PM*n*BE itself was insoluble. This difference in solubility would enable pattern formation of PM*n*BE by RDP.

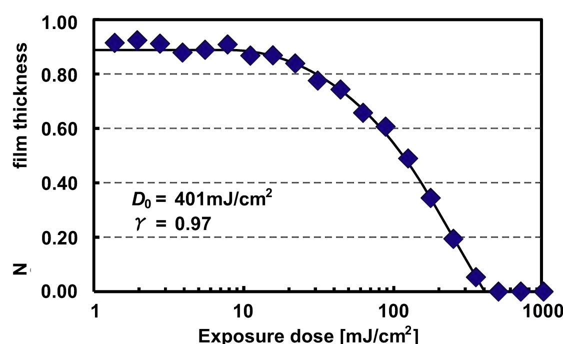


Fig. 2 Sensitivity curve of photosensitive PM*n*BE with 20 wt% of BADNQ3.
Development: TMAH/H_2O/NMP/MeOH = 2/5/5/18 (by weight), 50 °C/ultrasonication.

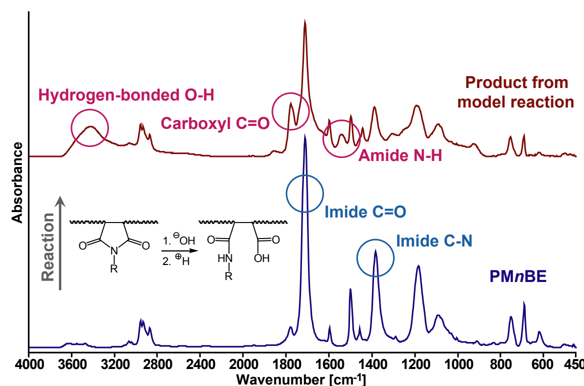


Fig. 3 IR spectra of PM*n*BE and the reaction product

Conclusions

Pattern formation of photosensitive imide-containing vinyl polymers based on RDP was realized by using OH^- of tetramethylammonium hydroxide (TMAH) as a nucleophile in developer. It was revealed that the key reaction of this pattern formation was ring-opening reaction of imide groups in polymer side chains during development. This pattern-forming mechanism is distinctly different from existing ones where important reactions (such as photo-induced cross-linking and acid generation, chemical amplification by post-exposure baking, etc.) occur before development, and expected to be applicable to other vinyl polymers with carboxylic-acid-derivative side chains.

References

1. Polymers for Microelectronics and Nano- electronics; Lin, Q.; Pearson, R. A.; Hedrick, J. C., Eds.; *ACS Symposium Series* 874, American Chemical Society: Washington DC, 2004.
2. K. Fukukawa, M. Ueda, *Polym. J.*, **40**, 281 (2008).
3. T. Fukushima, Y. Kawakami, A. Kitamura, T. Oyama, M. Tomoi, *J. Microlith. Microfab. Microsyst. (JM^3)*, **3**,159 (2004).
4. T. Oyama, S. Senoo, M. Tomoi, A. Takahashi, *J. Photopolym. Sci. Technol.*, **25**, 523 (2011).
5. J. M. Barrales-Rienda, J. I. Gonzalez de la Campa, J. G. Ramos, *J. Macromol. Sci., Chem.*, **A11**, 267 (1977).
6. M. El-Guweri, P. Hendlinger, A. Laschewsky, *Macromol. Chem. Phys.*, **198**, 401 (1997).