A alkaline developable, negative-type photosensitive poly(benzoxazole) based on poly(o-hydroxy amide), a novel activated ester-type cross-linker, and a photobase generator

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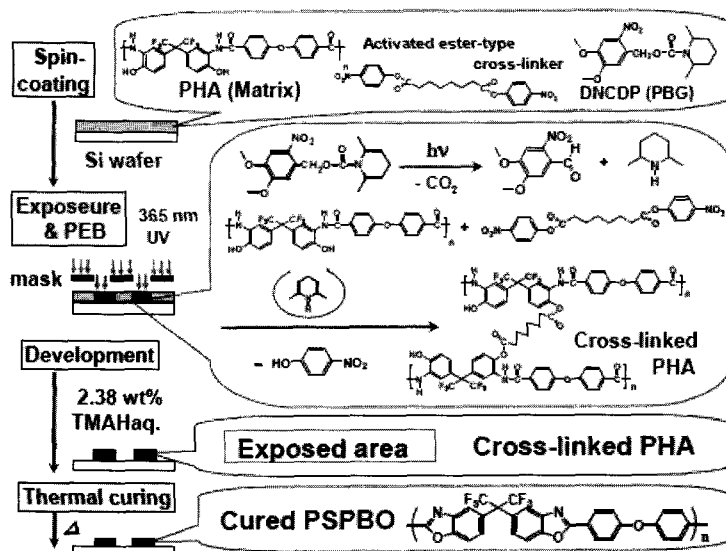Tokyo Institute of Technology 2-12-1-H120, O-okayama, Meguro-ku, Tokyo 152-8552, Japan
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Introduction

Poly(benzoxazole)s (PBOs) have been widely applied in the micro-electronic industry as insulating matrixes because of to their high thermal stability and excellent mechanical properties, and relatively low dielectric constants.[1-3] Especially, a photosensitive PBO (PSPBO) has been developed to simplify the pattern-formation processes, where phenolic hydroxyl groups in poly(o-hydroxy amide) (PHA) as a precursor of PBOs provide suitable solubility to an aqueous alkaline developer such as tetramethylammonium hydroxide aqueous solution (TMAHaq). Broadly, PSPBOs are formulated by both PHA and photoactive compound (PAC) diazonaphthoquinone (DNQ) as a dissolution inhibitor, which converts indene carboxylic acid as a dissolution promoter to alkaline developer after irradiation. Recently, the chemically amplified type PSPBOs have been developed to improve the sensitivity of PSPBO resist, where the PHA is combined with a cross-linker or a dissolution inhibitor and a photoacid generator (PAG).[2-6] However, they have a problem such as corrosion of metal (e.g., Al, Cu, Au etc) circuits in micro-tips by their acidic derivatives from PAG and DNQ. To overcome this problem, a novel photo-image formation is strongly demanded by using a photobase generator (PBG) instead of PAG for the next generation Photosensitive polymer resist. Here, we report the alkaline developable, negative-tone PSPBO based on PHA, a activated ester-type cross-linker, bis(p-nitrophenyl) suberoylate (BNPS), and a PBG {[(4,5-dimethoxy-2-nitrobenzyl)oxy] carbonyl}2,6-dimethyl piperidine (DNCDP), which generates 2,6-dimethylpiperidine (DMP) as a base after i-line (a filtered super-high-pressure mercury lamp : 365 nm UV light) irradiation. The patterning process using this PSPBO resist is shown in Scheme 1.

Scheme 1. PSPBO resist formuration system

Experimental

Materials

The matrix polymer, PHA derived from 4,4'-(hexafluoroisopropylidene)bis (*o*-aminophenol) (6FDA) and 4,4'-oxydibenzoyl chloride was prepared as described previously.[7] DNCDP was prepared according to the reported procedure in a 75 % yield after recrystallization from cyclohexane/hexane. m.p.:139.2 °C (literature: 122-124 °C).[8] TMAHaq was used as a base developer. *N*-methyl-2-pyrrolidinone (NMP:Wako), *p*-nitrophenol (TCI), acetyl chloride (TCI), triethylamine (TEA:TCI), suberoyl chloride (TCI), *p*-nitrophenyl acetate (NPA: TCI), other reagents and solvents were obtained commercially and used as received.

Instrumentation

The ^{1}H spectra were obtained on a BRUKER DPX-300 spectrometer at 300 MHz. Deuterated chloroform and dimethylsulfoxide were used as a solvent with tetramethyl silane as an internal standard. Number- and weight-average molecular weights (M_n and M_w) were estimated by a gel permeation chromatograph (GPC) on a Jasco co-2065 Plus system equipped with a polystyrene gel column (TOSOH TSKgel GMH$_{HR}$-M) eluted with THF at a flow rate of 1.0 mL/min calibrated by standard polystyrene samples. Thermal analysis was performed on a Seiko EXSTER 6000 at a heating rate of 10 °C/min for thermogravimetry (TG/DTA) under nitrogen. The film was spin-coated on a silicon wafer from the polymer solution in cyclopentanone, and the film thickness was measured by Veeco Instrument Dektak^3 surface profiler. The scanning electron microscopic image (SEM) was taken by a Technex Lab. Tiny-SEM 1540 with 5 kV accelerating voltage.

Synthesis of PHA

To a solution of lithium chloride (0.52 g, 12.3 mmol) and 6FDA (2.09 g, 5.70 mmol) in anhydrous NMP (11.2 g) was added 4,4'-oxydibenzoyl chloride (1.65 g, 5.59 mmol). The solution mixture was stirred at 0 °C for 30 min, then at room temperature for 20 h. After that, the solution was poured into (methanol/ water =100/800 mL) to precipitate a white powder. The precipitated solid was collected and dried in vacuo at 40 °C for 8 h. The yield was 3.19 g (97 %). IR (KBr,νcm^{-1}) 3425 (O-H), 1651 (C=O). ^{1}H NMR (DMSO-d_3, δ ppm): 10.2 (s, 2H), 9.51 (s, 2H), 8.02, 8.04 (d, 4H), 7.93 (s, H), 7.18, 7.20 (d, 4H), 7.00 (s, 4H). M_n= 9,700. M_w= 20,800.

Model reaction

PHA (60 wt %: 36.1 mol %), *p*-nitro-phenyl benzoate (NPA) (25 wt %: 48.8 mol %), and DNCDP (15 wt %: 15.1 mol %) was dissolved in cyclopentanone (Solid content: 18.3 wt %). The 1.1 µm film was prepared by spin-coating to prepare the film on a silicon wafer, following that prebaked at 80 °C for 30 sec, exposed with *i*-line of 500 mJ/cm^2, and post-exposure baked (PEB) at 140 °C for 1, 3 min. The film before and after irradiation was measured by FT-IR spectroscopy.

Synthesis of BNPS

To a solution of suberoyl chloride (3.0 g, 14.2 mmol) and p-nitrophenol (4.35 g, 31.3 mmol) in anhydrous THF (80 mL) was dropwised with TEA (4.31 g, 42.6 mmol) in THF (20 mL) at 0 °C. The solution mixture was stirred at 0 °C for 30 min, and at room temperature for 20 h. After that, the generated salt was removed by filtration, and the solution was concentrated by a rotary evaporator under reduced pressure, and then poured into water (500 mL) to yield a white powder. The precipitate was collected and recrystallized from ethyl acetate/n-hexane (1/4 volume ratio) to give the white plate product. The yield was 5.80 g (98 %). M.p. (114.5 °C: measured by DTA). IR (KBr,v,cm^{-1}) :1751 (C=O) , 1535 and 1342 (NO$_2$), 864 (C-N). ^{1}H NMR (CDCl$_3$-d_3, δ ppm): 8.22-8.27 (d,4H), 7.29-7.24 (d,4H), 2.59-2.64 (t,4H), 1.78-1.83 (m,4H), 1.48-1.53 (m,4H).

Dissolution Rate

PHA (M_n=9,700, M_w=20,700) was dissolved in cyclopentanone, followed by addition of BNPS (5 wt %) and DNCDP (5, 10, 15 wt %) (solid content: 19.6 wt %). The 1.1 μm thickness of polymer films were obtained by spin-casting from the solution on a silicon wafer. These films were pre-baked at 80 °C for 30 sec and then exposed to i-line by PEB temperature (100-180 °C) for each time. The dissolution rate (Å/sec) of the film thickness was determined from the changes in the film thickness before and after development with 2.38 wt % TMAH aq.

Photosensitivity

The photosensitive polymer solution was prepared by dissolving PHA, BNPS and DNCDP in cyclopentanone. The films were prepared by the spin-casting of this solution onto the silicon wafer. The films were subjected to a successive process as follows: pre-baking at 80 °C for 30 sec, exposure of i-line with changing a dose, PEB at 140 °C for 10 sec, and then developed with a base developer 2.38 wt % TMAHaq for 50 sec at room temperature. A characteristic photosensitive curve was obtained by plotting a normalized film thickness against exposure dose (unit: mJ/cm^2). Image-wise exposure through a mask was carried out in a contact-printing mode.

Results and Discussion

Model reaction

To investigate the a base-catalyzed trans-esterfication of PHA with NPA, the film consisting of PHA, NPA, and DNCDP was exposed to i-line, and then post exposure baked at 140 °C for 3 min. The films before and after aforementioned treatment were analyzed by FT-IR. The absorption of ester carbonyl group (C=O: 1776 cm^{-1}) in NPA on the exposed film disappeared, and the new peak assigned to the ester carbonyl group formed from the reaction of PHA and NPA appeared at 1751 cm^{-1}. On the other hand, the ester carbonyl group at 1751 cm^{-1} in the unexposed film was not detected at all. These behaviors in the exposed area imply that the trans-esterification of PHA with NPA occurs by a catalyst

DMP generated from PBG. Therefore, this transformation is applicable for a new image formation in a chemically amplified, negative-type PSPBO resist.

Synthesis of matrix polymer PHA

PHA s were prepared from 6FDA and 4,4'-oxydibenzoyl chloride in NMP in the presence of lithium chloride as a base at room temperature according the reported procedure. The Mns of two PHAs determined by GPC in THF at 40 °C were 9,700 (M_w/M_n = 2.14) and 13,200 (M_w/M_n = 2.43) with polystyrene standards.

Synthesis of a novel cross-linker BNPS

As a base-catalyzed cross-linker, BNPS was prepared from suberoyl chloride and p-nitrophenol in a quantitative yield as shown in Scheme 2. BNPS shows a good solubility in a wide variety of organic solvents due to a flexible aliphatic spacer. In addition, a clear transparent film could be spin-coated on a silicon wafer from a solution of PHA and BNPS in cyclopentanone.
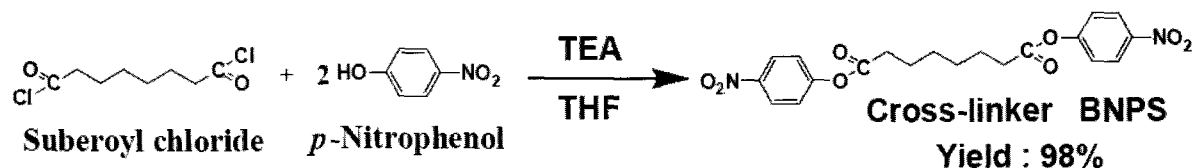

Scheme 2. Synthesis of a novel cross-linker BNPS.

Lithographic Evaluation of PSPBO with PBG

DNCDP, which has a strong absorption centered at 350 nm and allows using a 365 nm exposure, was chosen as a PBG. DNCDP generates 2,6-dimethylpiperidine (DMP) as a base catalyst after i-line irradiation. Moreover, DNCDP is a thermal stable PBG and the thermal decomposition temperature is at around 200 °C in the air.

The negative-working PSPBO resist system based on PHA, a cross-linker BNPS, and the PBG was formulated as shown in Scheme 3.
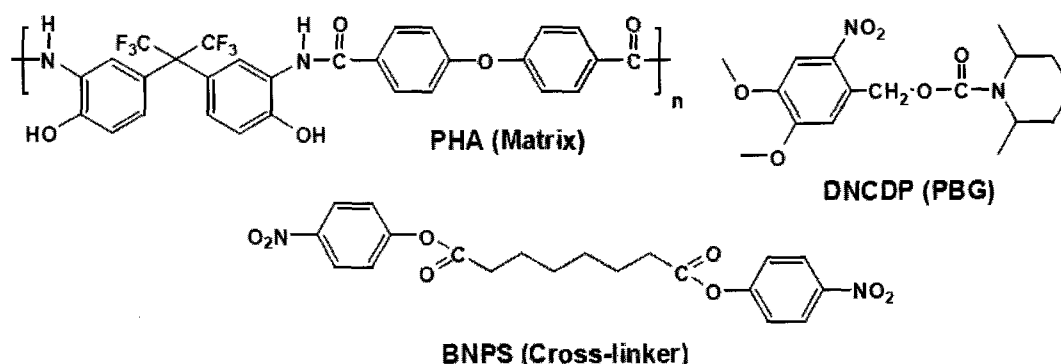
Scheme 3. Formulation of photosensitive polymer

The films spin-cast on a silicon wafer were prepared, exposed by *i*-line, and developed with a 2.38 wt % TMAHaq at room temperature. The dissolution rate was calculated by measuring the change of the film thickness before and after development. The PEB temperature and time are crucial for the chemically amplified resist system because the diffusion of the base generated from PBG after *i*-line exposure in the films is an important key factor.
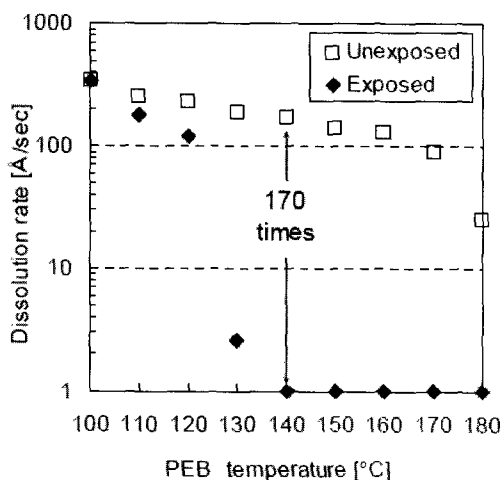

Figure 1. Effect of PEB temperature on the dissolution rate for the PSPBO films (PHA/BNPS/DNCDP:80/5/15 wt %, film thickness: 1.1 μm) in the exposed (◆) and unexposed areas (□). The *i*-line exposure and PEB time were fixed at 300 mJ/cm² and 10 sec, respectively, and developed in 2.38 wt % TMAHaq.
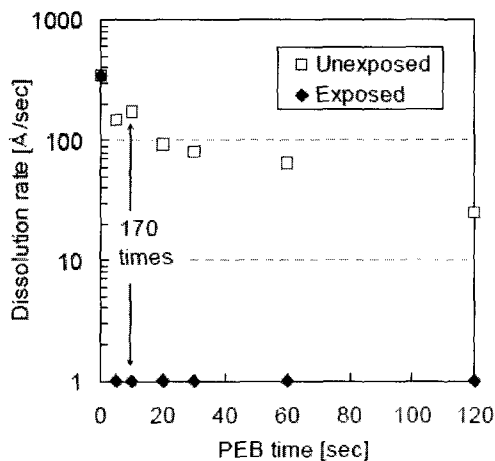
Figure 2 Effect of PEB time on the dissolution rate for the PSPBO films (PHA/BNPS/DNCDP: 80/5/15 wt %, film thickness: 1.1 μm) in the exposed (◆) and unexposed areas (□). The *i*-line exposure and PEB temperature were fixed at 300 mJ/cm² and 140 °C, respectively, and developed in 2.38 wt % TMAHaq.

First, the effect of PEB temperature on the dissolution rate in 2.38 wt % TMAHaq was studied, where each film was pre-baked at 80 °C for 30 sec in the air, exposed to 300 mJ/cm² of *i*-line, and then post-exposure baked at each temperature for 10 sec. The results are shown in Figure 1. An enough dissolution contrast (DC) (170 times) is obtained at PEB temperature 140 °C, probably because DNCDP (m.p.=139 °C) worked as a plasticizer over around 130 °C to totally enhance the mobility of the resist film. Hence, the base 2,6-dimethylpiperidine generated from PBG can diffuse effectively in the film at this temperature in short time (10 sec) and accelerates the cross-linking reaction as shown in Figure 2. Next, the effect of DNCDP loading was investigated with a 5 wt % BNPS loading. The results shown in Figure 3 indicate that a 15 wt % DNCDP loading is necessary to get a high DC. This is because the quantum yield of 3,4-dimethoxy-6-nitrobenzyl derivatives are not high.[9]

On the basis of these findings described above, a resist system consisting of PHA (80 wt %: 70.9 mol %), BNPS (5 wt %: 6.9 mol %), and DNCDP (15 wt %: 22.2 mol %) was formulated. The

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characteristic photosensitivity curve of a 1.1 μm resist film indicates the good sensitivity ($D_{0.5}$) of 78 mJ/cm² and the good contrast ($\gamma_{0.5}$) of 4.0, respectively as shown n Figure 4. Ultimately, Figure 5 shows a SEM image of a contact-printed pattern after exposure of *i*-line through a photo-mask. The resist is capable of resolving a 6 μm feature when a 2.5 μm thickness film was used. The printed pattern was converted to the resulting PBO pattern by heating at elevated temperature up to 350 °C for 1h under nitrogen. The formation of the PBO was confirmed by the IR spectra. where the characteristic C-O absorption at 1049 cm⁻¹ and the absorption due to the carbonyl group of amide bond disappeared at 1651 cm⁻¹ in the PHA.
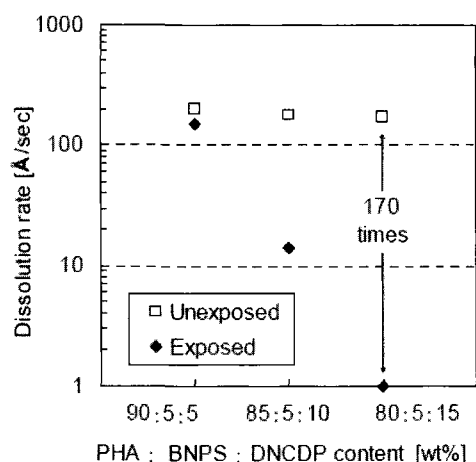

Figure 3. Effect of DNCDP loading on PSPBO at 140 °C for 10 sec on the dissolution rate for the PSPBO films (BNPS: 5 wt %, film thickness: 1.1 μm) in the exposed (◆) and unexposed areas (□). The *i*-line exposure, PEB temperature and PEB time were fixed at 300 mJ/cm², 140 °C and 10 sec. respectively, and developed in 2.38 wt % TMAHaq.
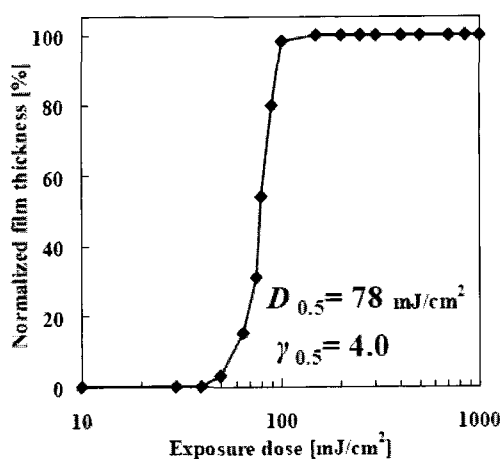
Figure 4. Characteristic photosensitive curve of a PSPBO:PSPBO films (PHA/BNPS/DNCDP : 80/5/15wt%).The PEB temperature, PEB time, and develop-ment time in 2.38 wt % TMAHaq were fixed at 140 °C,10 sec. and 50 sec. respectively. $D_{0.5}$ is the sensitivity, and $\gamma_{0.5}$ is the contrast.
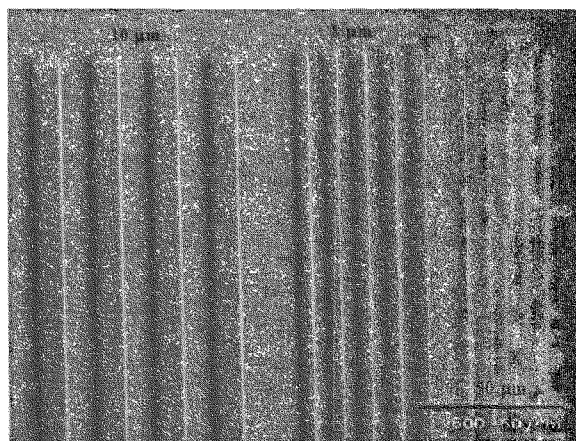

Figure 5. SEM image of the negative-pattern 2.5 μm-thick film (PHA / BNPS / DNCDP : 80 / 5 / 15 wt %). The M_n and M_w of PHA as a matrix were 13,300 and 32,100. respectively. The lithographic condition was as follows; 22.2 wt % solid content solution in cyclopentanone was spin-coated, prebaked at 80 °C for 30 sec, exposed 150 mJ/cm² of *i*-line, post-exposure baked at 140 °C for 10 sec. developed with 2.38 wt % TMAH aq for 98 sec at room temperature.

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Conclusions

To remedy corrosion of metals circuits in micro-tips by the acidic derivatives from PAG and DNQ, the novel negative-type PSPBO resist consisting of PHA, BNPS as a cross-linker, and PBG DNCDP has been developed. The chemically amplified, negative type PSPBO based on PHA (80 wt %), BNPS (5 wt %) and DNCDP (15 wt %) showed the high sensitivity ($D_{0.5}$) of 78 mJ/cm^2 and the good contrast ($\gamma_{0.5}$) of 4.0, respectively. After the optimization of photolithographic evaluation, a fine negative pattern with a 6 µm line and space was obtained in a 2.5 µm film on the silicone wafer. Furthermore, this PHA pattern film was converted to PSPBO by thermal treatment up to 350 °C. This PSPBO formulation system can be a candidate for the next-generation resist.

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