Novel Positive-tone Photosensitive Polyimide Based from Quantitative Partial Esterified Poly(amic acid)

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Introduction.

Polyimides are widely used for semiconductor applications such as inter-layer dielectrics, protection layers (buffer coatings), and re-distribution layers for wafer level package[1]. For these applications, polyimide is required to make a fine pattern by photo-lithographic technique. In order to simplify the polyimide pattering process, several groups developed the addition of photosensitivity to polyimide precursor namely PSPI[2,3]. Most of the PSPIs were negative tone type, which made exposed area insoluble by photo-reaction. In order to progress semiconductor, polyimide requires fine pattern such as 5μm or less. To realize such a fine pattern, positive-tone PSPI was desired. First positive-tone PSPI was reported by Loprest and McInerney[4]. The posi PSPI was composed of PAA and naphthoquinone diazide compound which is popular for novolak photo resist system. But it was not realized due to high solubility of PAA to alkaline solution. Many types of positive tone photosensitive polyimides were reported to overcome the problem[5-12].

On the other hand, Rubner reported positive tone photosensitive polybenzoxazole precursor[13]. Polybenzoxazole precursor was poly(hydroxyamide) which has phenolic groups in the polymer chain. The acidity of phenol group was much weaker than that of aromatic carboxylic acid. The dissolution of the poly(hydroxyl)amide is suitable for 2.38% tetramethyl-ammonium hydroxide (TMAH) solution. The positive tone photosensitive polybenzoxazole precursor was applied for buffer coating of semiconductor devices[14].

In order to obtain posi PSPI with wide process window, it was important to control the dissolution rate of the PAA to the 2.38% TMAH solution. In this article, we reported finding of novel partial quantitative esterification of PAA and the dissolution rate control to the alkaline solution. Novel positive photosensitive polyimide precursor was obtained by mixing with partial esterified PAA and naphthoquinone diazide sulfonate with solvents.

Experimental.

Materials: Oxydianiline (ODA) was obtained from Wakayama-seika. 3,3',4,4'-diphenylether tetracarboxylic acid dianhydride (ODPA) was obtained from Manac. N-methyl-2-pyrrodinone(NMP), and gamma-butyrolactone(GBL) were obtained from Mitsubishi-chemical. Dimethylformamide-dialkylacetals(DFAs) were purchased from Tokyo-kasei. All chemicals were used without any purification.

Polymerization of quantitative partial esterified poly(amic acid) (PAA): ODA (19.01g, 90mmole) was dissolved into 100mL of NMP in a 4 neck 500mL round bottom flask equipped with a

thermometer, a nitrogen inlet and a mechanical stirrer. After dissolving the diamines completely, ODPA (31.01g, 100mmole was added to the solution with 50mL of NMP. Then the solution was reacted at 40 ℃ for 2 hours. 3-Aminophenol (6.54g, 60mmole, Tokyo-Kasei) was added to the solution and reacted for 4hour at 50℃. After polymerization, N,N-dimethylformamide diethyl-acetal (30.63g, 190mmol, DFA, Tokyo-Kasei) was dropwised to the solution with 30ml of NMP to proceed esterification. The mixed solution was treated with stirring at 50℃ for 2h. Then, the solution was poured into 5L of deionized water. White polymer powder was collected by filtration. The powder was washed by water for 5 times. Then, the partial esterified poly(amic acid) powder was dried at 50℃ for 72hours under vacuo.

Synthesis of naphthpquinone diazide compound (Photo sensitive compound):

4,4'-[1-[4-[1-(4Hydroxyphenyl)-1-methylethyl]phenyl] ethylidene] bisphenol (21.23g, 50mmole, Tris-PA, Honshu-Kagaku) was dissolved into 200mL of 1,4-dioxane (Wako) in 500mL of 4neck flask equipped with a stirrer, a funnel, a nitrogen inlet and a thermometer. The solution was heated to 40℃ in a water bath. 5-Naphthoquinone diazide sulfonyl chloride (33.84g, 125mmol, NAC-5, Toyo-Gosei) was added to the solution. Then triethylamine (12.64g, 125mmol, Nakarai) was dropwised slowly by a funnel with 50mL of 1,4-dioxane. The solution was stirred for 2hrs at 40℃. Then the solution was filtered. The filtrate was poured into 2L of deionized water. Yellowish powder was precipitated. The yellowish powder was washed by 1% of HCl and then by water five times. The powder was collected by filtration. The naphthoquinone diazide compound powder was dried at 50℃ for 72 hours under vacuo.

Preparation of positive tone photosensitive polyimide solution:

The Positive photosensitive polyimide solution was prepared by mixing with 10g of partial esterified poly(amic acid), 2g of naphthoquinone diazide compound and 30ml of GBL. The mixture was filtered by 1um pore size poly(tetrafluoro-ethylene) filter (PF-010, Advantech).

Photosensitivity measurement:

The posi PSPI was coated on a 6inch Si mirror wafer at 2 μm after 120℃ baking by a spin coater (Mark-7, Tolyo-Electron). Then the coated wafer was soft-baked at 120℃ for 2min on a hot plate (Mark-7). The coated film thickness was measured by an optical interferometry method (STM-802, Dainippon Screen). The soft-baked wafer was exposed by i-line Stepper (GCA, DSW-8000) from $500J/m^2$ to $12000J/m^2$. The exposed wafer was developed by 2.38% of tetramethyl ammonium hydroxide solution (TMAH, Mithsubishi-Gas-Chemical).

After the development, the patterned wafer was cured at 320℃ for 30min by an inert oven (Koyo-thermosystem INH-9). The obtained posi-PSPI pattern was observed by an optical micro scope. A cross sectional view of the PSPI pattern was observed by a scanning electron microscopy (SEM). SEM photos were obtained by S-4800 (Hitachi) at 3KV of acceleration voltage. Posi-PSPI patterns on the Si wafer were sliced and sputtered by palladium to obtain cross sectional photos of the posi-PSPI.

Results and Discussion.

Polymerization of quantitative partial esterified poly(amic acid):

No one could not success to obtain quantitative partial esterification of poly(amic acid). This is the first example to control the carboxylic acid concentration in poly(amic acid)s. (Figure 1) DFA is known as an esterification reagent in gas-chromatography[16].

Effect of alkyl groups in DFAs were summarized in table 1. In case of lower alkyl groups, such as methyl or ethyl groups, the reaction conversion is almost 100% including imidization. So the reaction proceeds quite quantitatively. On the other hand, bulky alkyl group gives higher selectivity from imidization.

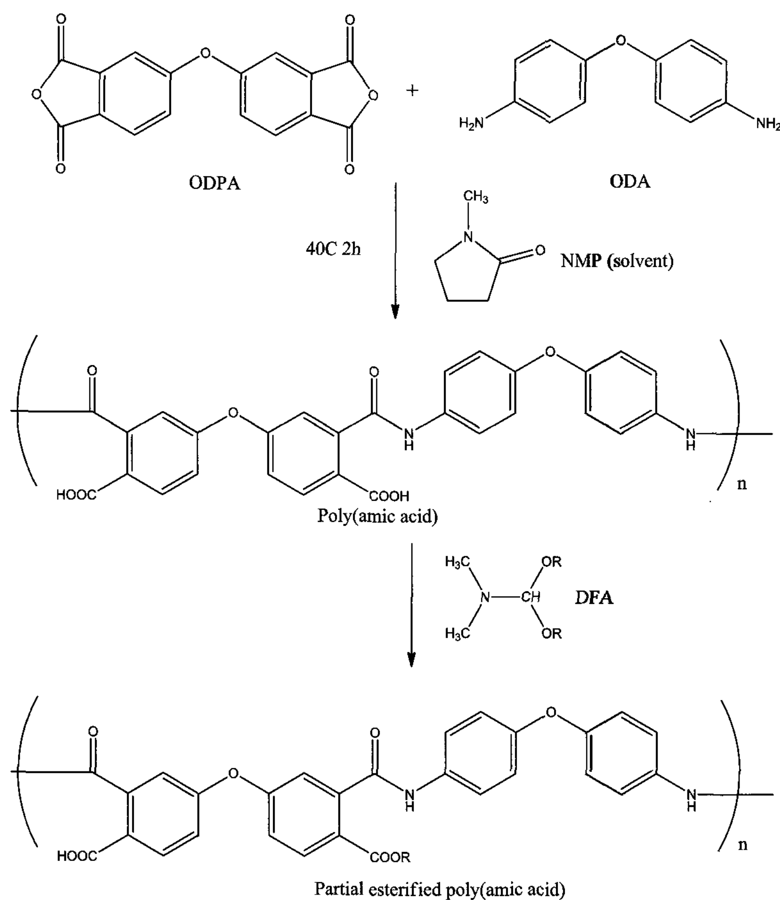
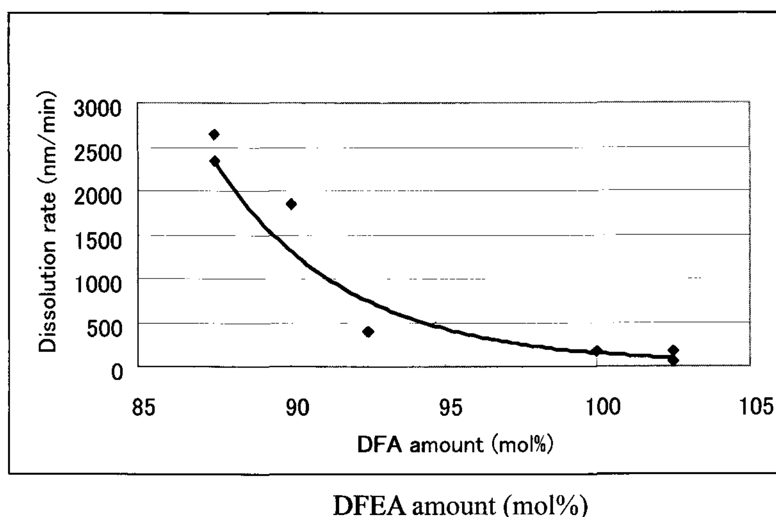


Figure 1. Reaction of quantitative partial esterification

Table 1. Effect of alkyl groups in DFAs

Alkyl group	Esterification	Imidization	Ester/imide ratio
Methyl	65%	30%	2.2
Ethyl	70%	25%	3.0
iso-Propyl	60%	10%	6.0
No treatment	0%	10%	–



DFEA amount (mol%)

Figure 2 DFEA amount dependency on dissolution rate of polyimide precursor
DFEA : N,N-dimethylformamide diethylacetal

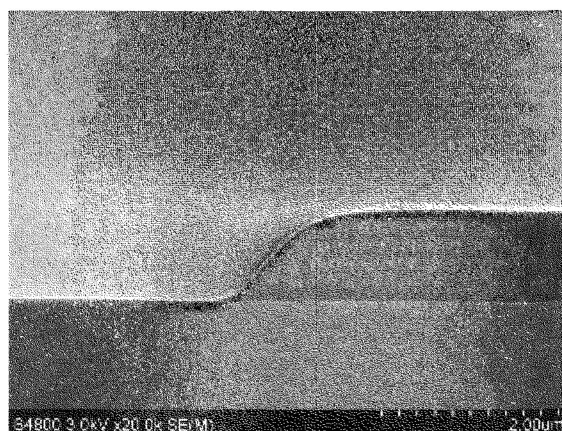


Figure 3 Cross sectional view of positive photosensitive polyimide pattern obtained by this study

As shown in figure 2, we can control the dissolution rate of partially esterified poly(amic acid) to 2.38% TMAH by changing the DFA amount. To obtain good positive tone photosensitive polyimide, dissolution rate of polyimide precursor is about 100-1000nm/min. From the figure 2, we could obtain the desired dissolution rate polyimide precursor by addition of 90-95mol% of DFEA.

Positive tone photosensitive polyimide (posi PSPI) was prepared by mixing the partial esterified poly(amic acid), naphthoquinone diazide compound and solvent. The obtained posi PSPI was coated on Si wafer by spin coating, pre-baked at 120C by hot plate, exposed by i-line stepper, and developed by 2.38% TMAH solution. As shown in figure 3, we obtained positive tone polyimide pattern. This is quite useful from the points of polymer reaction and industrial application.

Conclusions. We developed novel quantitative esterification of poly(amic acid) by using dimethylformamide-dialkylacetal. By using quatitatively partial esterification technique, we obtain novel positive photosensitive polyimide precursor by mixing with suitable dissolution rate polyimide precursor and naphthoquinone diazide sulfonate with solvents. This is quite useful to obtain the positive tone photosensitive polyimide from various types of poly(amic acid)s.

References(see p42)