A New Aqueous Developable Positive Tone Photodefinable Polyimide for a Stress Buffer Coat of Semiconductor; HD-8000

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A new aqueous developable positive tone photodefinable polyimide was prepared from poly(hydroxy amic acid) and naphthoquinonediazide for semiconductor stress buffer coat, which exhibits excellent photolithographic properties in high resolution, wide focus latitude and good stability for process holding time, with equivalent film properties to conventional non-photodefinable polyimide. Through dry etching evaluation of the SiN passivation layer, it was confirmed that the cured polyimide pattern works as an etching mask.

Keywords: polyimide, aqueous developable, positive tone, photodefinable

1. Introduction

In semiconductor manufacture, polyimides are applied on a wide range of devices as a passivation film (a stress buffer coat), because of their excellent thermal and mechanical properties [1]. Recently, the use of photodefinable polyimides (PDPIs), especially aqueous developable positive tone PDPIs, has been increasing. PDPIs can simplify pattern-defining processes in comparison with non-PDPIs. In addition, aqueous developable positive tone PDPIs are preferable to solvent developable negative tone PDPIs in virtue of the following benefits.

- Compatibility of process machines and reticles for photoresist.

- Scum less after development,

- Higher resolution,

- Less environmental concern in waste disposal,

To realize an aqueous developable positive tone PDPI, various systems have been proposed [2]-[12]. From the viewpoint of photodefinable mechanisms, these systems can be roughly classified into two groups: naphthoquinonediazide (NQD) systems and chemical amplification systems. We considered that the NQD system is more beneficial for an aqueous positive tone PDPI, because the NQD system needs no post exposure bake (PEB) and shows wider process margin.

For the NQD system, poly(amic acid)s (PAAs) [2][3], poly(hydroxy amic acid ester)s (PAEs) [4][5] and soluble poly(hydroxy imide)s (SPIs) [6][7] have been reported. A precursor of polybenzoxazole (PBO), which is not a polyimide but shows equivalent thermal and mechanical properties, has also been reported [6]. These were published independently, so it is difficult to ascertain which will be the most feasible for the purpose.

Figure 1 Polymer structures

We compared these polymers in their photolithographic, thermal and mechanical properties [13]. To standardize the comparison, the same moieties indicated by X and Y in Figure 1 were chosen. The PAA showed a low photolithographic contrast due to the less dissolution inhibition at the unexposed area; the contrast is defined as the dissolution rate ratio of the exposed area to the unexposed area. The contrast for the SPI was not high because of the low dissolution promotion at the exposed area. The PAE and the PBO precursor showed high contrasts and were expected to realize good photolithographic properties.

The cured film from the PAE formulation demonstrated no delamination by the cross-cut method after 500 hours of PCT (pressure cracker test: 121°C, 2 atm.), while the PBO film was peeled off only after 10 hours of PCT.

Based on the above results, a new aqueous positive tone PDPI consisting of PAE, HD-8000, was developed with the optimization of the NQD compound and the other additives for further improvement of photolithographic properties. In this paper, the photolithographic and film properties of HD-8000 are described.

2. Experimental

2.1. Materials

PAE was prepared from aromatic dianhydride and aromatic hydroxy diamine by acid chlorination method through esterification of aromatic dianhydride [14]. Photoactive compound was synthesized through the condensation of naphthoquinonediazide sulfonyl chloride and phenolic moieties. HD-8000 was prepared by dissolving the PAE, the NQD compound

and the other additives in a solvent, and then filtered through 0.2 µm pore-size Teflon filter.

2.2. Photolithographic evaluation

Typical process conditions of HD-8000 in the cured thickness range of 2 to 11 µm are shown in Table 1. (For the thickness of 2 to 4 µm, the lower viscosity version, HD-8001, is used.)

2.3. Film properties and adhesion

Sample specimens for the measurement of film properties were prepared on silicon wafers under the conditions shown in Table 1.

Adhesion to substrates as a function of PCT (121°C, 2atm.) time was examined by the cross-cut method (JIS K-5400) for the films cured in the same manner.

Adhesion strength to molding compounds was measured by the stud-pull method after 168hr of accelerated test (85°C, 80%RH); the molding compound was formed into a stud of 3.65 mm in diameter on the cured HD-8000 film.

2.4. Dry etching tolerance

Dry etching conditions are shown in Table 2. The etching rate of HD-8000 was calculated from the reduced film thickness through dry etching.

Table 2 Dry etching conditions

Item	Unit	Condition
Machine	-	Ulvac CSE-1110
Pressure	Pa	10
RF power	W	100
Gas	-	CF ₄ /O ₂ * ¹
Gas flow rate	sccm	25

*1: Ratio of CF₄ to O₂ was varied.

Table 1 Typical process conditions

Process	Units	Target cured thickness (µm)					Reagent
		2	4	5	8	11	
		HD-8001		HD-8000			
Coating	Pre-spin	rpm/sec	1000/5				HD-8000
	Spin	rpm/sec	4000/30	2200/30	3400/30	1900/30	-
	Pre-bake	°C/sec	120/100	120/120	120/130	120/180	120/260
	Pre-baked thickness	µm	3.6	7.3	9.4	14.7	18.7
Exposure	Dose	mJ/cm ²	180	250	250	500	700
Development	Puddle 1	sec	15	32	35	60	90
	Puddle 2	sec	15	32	35	60	90
	Rinse	rpm/sec	1000/10				DI water
	Spin dry	rpm/sec	3500/10				-
	Developed thickness	µm	2.7	6.0	7.2	11.5	15.1
Post-bake	Ramp up	°C/min	150-350/60				N ₂ flow
	Hold	°C/min	350/30				
	Cured thickness	µm	2.0	4.2	5.1	8.2	10.9

3.Results and Discussion

3.1. Photolithographic properties

Photolithographic properties were evaluated for 5, 8 and 11 μ m cured thickness. Sensitivity curves of HD-8000 are shown in Figure 2. The measure of sensitivity, E_{th} for 5, 8 and 11 μ m cured thickness are 200, 350 and 580 mJ/cm², respectively. In practical use, exposure dose in 20 ~ 40 % excess of E_{th} will be recommended to have enough process margin.

Cross-sections of HD-8000 after development and after cure are shown in Figure 3. There is no scum observed in space area after development. This is a distinctive feature of HD-8000 in comparison with solvent developable negative tone PDPIs.

Figure 4 shows the mask linearity for each of the three cured thickness. Good linear correlations are exhibited between mask sizes and pattern critical dimensions for 5,

8 and 11 μ m cured thickness to 2; 4 and 4 μ m, respectively.

Figure 2 Sensitivity curves of HD-8000 for 5, 8 and 11 μ m cured thickness.

Figure 3 Cross sections of HD-8000 patterns for 5, 8 and 11 μ m thickness cured

Figure 4 Mask linearity of HD-8000

Figure 6 Dependence of critical dimension on focus

(1) +3 μm

(5) -1 μm

(2) +2 μm

(6) -2 μm

(3) +1 μm

(7) -3 μm

(4) 0 μm

Figure 5 Focus latitude of HD-8000 (Stepper numerical aperture was 0.24.)

PDPIs need to have a wide focus margin, because semiconductor devices just before applying PDPIs have a few microns of trench and stepped topologies. The cross-sections of HD-8000 after development for varied focus values are shown in Figure 5. HD-8000 did not show significant changes in the pattern profile in -3 to $+3$ μm focus range. Figure 6 shows the dependence of critical dimension on focus for variations of exposure dose. Critical dimension at each exposure dose showed less dependence on focus of -3 to $+3$ μm .

Figure 7 shows the stability of E_{th} and film retention after development for process holding time. Both E_{th} and film retention are stable for over 70 hours of time between pre-bake and exposure. The stability for the hold time between exposure and development is also kept for over 70 hours.

3.2. Film properties

Film properties of HD-8000 are summarized in Table 3 with referring to those of PIX-3400, which is a typical non-photodefinable polyimide and has been widely employed in semiconductor manufacture. HD-8000 demonstrated film properties almost equivalent to PIX-3400.

The adhesion of HD-8000 was evaluated for six kinds of substrate: Si, SiO, SiN, Al, Ti and SiNO. The results of the cross-cut method before and after PCT are shown in Table 4. No delamination was observed even after 1000 hours of PCT on all kinds of substrates tested.

Table 5 shows the adhesion strength to molding compounds. HD-8000 demonstrated stronger adhesion than PIX-3400 to any of following three kinds of molding compounds: cresol-novolac, biphenyl and dicyclo types.

(1) Pre-bake - exposure

(2) Exposure - development

Figure 7 Stability of E_h and film retention for process hold time

Table 3 Film properties of HD-8000

Item	Measurement method	Unit	HD-8000	PIX-3400*1
Tg	TMA	°C	300	295
CTE		ppm/°C	47	55
Tensile strength	Autograph	MPa	122	114
Elastic modulus		GPa	2.5	2.1
Elongation		%	23	22
1% Weight loss temp.	TGA	°C	403	450
5%		°C	433	531

*1: Typical non-photodefinable polyimide

Table 4 Adhesion to substrates

PCT time	Si	SiO	SiN	Al	Ti	SiNO
0 hr	100/100	100/100	100/100	100/100	100/100	100/100
100 hr	100/100	100/100	100/100	100/100	100/100	100/100
300 hr	100/100	100/100	100/100	100/100	100/100	100/100
500 hr	100/100	100/100	100/100	100/100	100/100	100/100
1000 hr	100/100	100/100	100/100	100/100	100/100	100/100

*X/100 means that X square pieces among 100 pieces did not peel off after the cross-cut test.

Table 5 Adhesion to molding compounds

Molding compound	Unit	HD-8000	PIX-3400
Cresol-novolac type	kgf/10.2 mm ²	6.4	4.5
Biphenyl type	kgf/10.2 mm ²	4.6	3.2
Dicyclotype	kgf/10.2 mm ²	3.8	2.0

(1) Dry etch rates of HD-8000 and SiN

(2) Selectivity of HD-8000

Figure 8 Dry etch tolerance of HD-8000

Figure 9 Dry etching of SiN layer with HD-8000 mask

*Spacewidth of HD-8000 pattern is 5 μm .

On the Basis of the results shown in Table 3 to 5, HD-8000 is expected to exhibit the reliability equivalent to PIX-3400.

3.3. Dry etching tolerance

Owing to high resolution under 5 μm , HD-8000 can be used as a dry etching mask for passivation layers. This allows the elimination of photoresist process for the dry etching. Figure 8 shows the dry etching tolerance of cured HD-8000 and silicon nitride (SiN). The etching selectivity, which is defined as the ratio of etching rates of SiN to HD-8000, shows a maximum at 75/25 of CF_4/O_2 gas composition. As shown in Figure 9, the dry etching of SiN layer at this gas composition was demonstrated with the mask of cured HD-8000. The SiN layer of 5 μm width space was clearly etched, while HD-8000 pattern seemed almost the same.

4. Conclusion

We have developed a new aqueous positive tone photodefinable polyimide, HD-8000, for semiconductor stress buffer coats, inter layer dielectrics and the like. HD-8000 has good photolithographic properties: high resolution, wide focus margin and high stability for process holding time. HD-8000 exhibits film properties almost equivalent to non-photodefinable polyimide and also excellent adhesion to substrates and molding compounds. Cured patterns of HD-8000 can be used as a dry etching mask for the passivation layer of SiN.

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