新規な感光性低CTE材料の開発

Development of New Photosensitive Low CTE Materials

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シリコン貫通電極（TSV）などの3次元実装を実現するためには，小型化，高周波動作，消費電力の低減などの観点から，極薄シリコンウエハの使用が必須となっている．このようなウエハ上に従来の既存材料を塗布して硬化させると，材料とウエハの線膨張係数（CTE）の不一致に起因する残留応力や反りが発生し，製品の信頼性低下が懸念される．一方，低CTEを示す材料として高温硬化型感光性ポリイミドが知られているが，硬化時の高温によって耐熱性の低い基板や他の材料などへのダメージが懸念される．そこで著者らは，低温硬化可能な感光性低CTE材料の開発に着手した．分子設計に従って樹脂を合成，評価を行った結果，260 ℃で硬化することで低CTE，低残留応力，高耐熱性を示し，かつ良好なリソグラフィ性能を示す感光性材料ROD-100を開発した．

To realize three-dimensional (3D) packaging such as Through-Silicon Via (TSV), ultrathin silicon wafers are required for downsizing, high-frequency operation and reducing power consumption. When conventional existing materials are coated onto such wafers and cured, residual stress and warpage arising from the coefficients of thermal expansion (CTE) mismatch between materials and wafers deteriorate reliability of products. On the other hand, high temperature-curing type photosensitive polyimides (PSPIs) have low CTE, but there are concerns about damage to low heat resistant substrates and other materials. Therefore, we started development of low temperature-curing type photosensitive low CTE materials. Resins were synthesized according to the molecular designs, and evaluated. As a result, we succeeded in development of the material, ROD-100, which has low CTE, low residual stress and good heat resistance by curing at 260 °C. And it also shows good lithography performance.

1 Introduction

Silicon-based semiconductor integrated circuits have been highly developed towards miniaturization and high integration according to Moore's Law [1), 2)]. However, it was believed that within several years the further miniaturization may reach its limit because of physical and economical factors. Recently, TSV technology has been actively developed to realize 3D packaging, basing on the idea that high integration can be accomplished by mounting chips sterically [3)]. Accordingly, ultrathin wafers are required for downsizing, high-frequency operation and reducing power consumption. The wafer thickness for 3D packaging will be reduced to around 5 μm, as indicated by ITRS 2011 [4)].

Most of existing materials have CTE within the range of 40 to 80 ppm/°C, which are much higher than that of silicon wafer (4 ppm/°C) and copper wiring (17 ppm/°C). When such existing materials are coated onto silicon wafers and cured, residual stress and warpage arising from the CTE mismatch between materials and wafers deteriorate reliability of products. Therefore, photosensitive low CTE materials such as negative and

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positive type PSPIs have been studied to solve this problem[5),6)].

Figure 1 shows correlations of CTE (vertical axis) and curing temperature (horizontal axis). Conventional existing materials are on the trade-off line in the figure. For example, high temperature-curing type PSPIs have low CTE (about 20 ppm/°C). It is known that low CTE strongly depends on rigidity and orientation of the molecular backbone. On the other hand, the PSPIs require high curing temperature, typically more than 300 °C, for cyclization. Because of the high temperature, there are concerns about damage to low heat resistant substrates and other materials[7)]. Therefore, we started development of low temperature-curing type photosensitive low CTE materials. Properties and molecular designs of the base resin are outlined in Figure 2.

Resins were synthesized according to the molecular designs, and evaluated. As a result, we succeeded in development of the low temperature-curing type photosensitive low CTE material, ROD-100, which has good

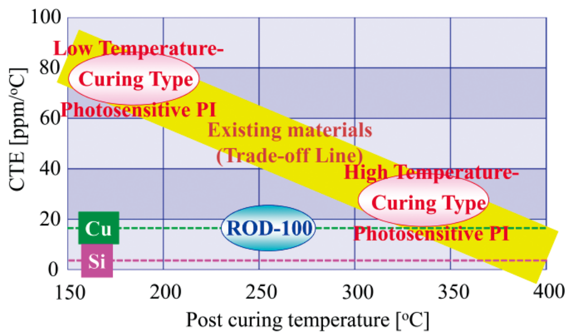


Figure 1 Correlations of CTE and curing temperature.

Properties	Molecular designs
Lithography performance	Introduction of alkali-soluble groups such as naphthalene polyols
Low temperature-curing	Heat reactivity of the base resin at low temperature
Low CTE and low residual stress	Rigidity and orientation

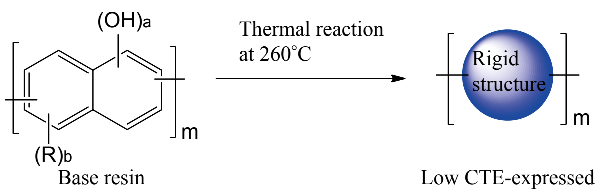


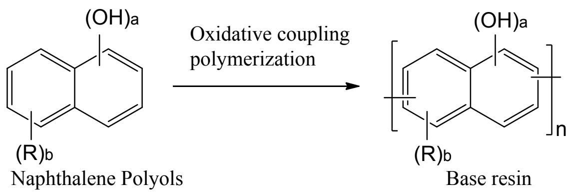
Figure 2 Properties and molecular designs to give to the base resin.

properties beyond the trade-off line as shown in Figure 1. In this paper, we report on validity of the molecular designs and the data of film properties and lithography performance.

2 Experimental

2.1 Synthesis of resins

At first, we focused on the certain kind of naphthalene polyols having rigidity and alkali-solubility as a monomer. Because naphthalene polyols exist in several position isomeric forms, resins were prepared by oxidative coupling polymerization of each isomer as shown in Scheme 1. Mw and given properties of the resins are summarized in Table 1.



Scheme 1 Synthesis of resins.

Table 1 Mw and given properties of the resins

Resin	Mw	Rigidity	Heat reactivity	Alkali-solubility
A	50,000	○	○	○
B	36,000	△	△	○
C	17,000	△	○	○
D	20,000	×	○	○

Table 2 Standard process conditions for evaluation of ROD-100

Process	Conditions
Primer treatment	3-Aminopropyltrimethoxysilane 150 °C/5 min
Film thickness	3 μm (For lithography) 10 μm (For film properties)
Prebake	90 °C/3 min
Exposure (g, h, i-line mixed)	500 mJ/cm^2 (3 μm) 1,000 mJ/cm^2 (10 μm)
Post exposure bake	95 °C/7.5 min
Development	60 sec/2.38 wt% TMAH
Rinse	60 sec/DI water
Post cure	30 °C -> 260 °C/60 min, under N_2 atmosphere (Rate : 10 °C/min)

2.2 Preparation of the photosensitive resin composition

The photosensitive resin varnish was prepared by adding the resin, the crosslinking agent and the photo acid generator (PAG) to mixed solvent of Ethylene glycol monomethyl ether (EGME) and Propylene glycol monomethyl ether acetate (PGMEA).

2.3 Preparation of cured films

Table 2 shows standard process conditions to evaluate film properties and lithography performance.

2.4 Evaluation methods of thermal, mechanical and adhesion properties

Evaluation methods of thermal, mechanical and adhesion properties are summarized in Table 3.

2.5 Evaluation of chemical resistance

Cured films on silicon wafers were immersed in test solvents at room temperature for 10 min. After that the films were washed with water and dried at room temperature. By the film thickness measurement before and after dipping, the change ratio was calculated. In addition, the appearance was observed with an optical microscope.

3 Results and Discussion

3.1 Resin screening

We compared residual stress and CTE of the resins **A**-**D** without any additives. Films were prepared by curing at 260 °C for 60 min after prebaking. The results are summarized in Table 4.

The resin **A** which satisfied all molecular design items showed the lowest residual stress and CTE. As a result, validity of the molecular design was confirmed. Table 5 shows various properties of the resin **A**.

The resin **A** exhibited good solubility for alkali developing solution (2.38 wt% TMAHaq). The cured film showed not only low CTE and low residual stress, but also good heat resistant. Then we prepared the photosensitive resin composition, and evaluated as a negative type resist, ROD-100.

3.2 Film properties

Thermal properties, mechanical properties and residual stress of the resin composition are summarized in Table 6.

The CTE of ROD-100 was 18 ppm/°C, and it was

Table 3 Evaluation methods of film properties

Items	Methods
Glass Transition Temperature (Tg)	TMA method
CTE (-65 °C <-> 150 °C)	TMA method
Thermal Decomposition Temperature	TGA method 10 °C/min in N_2
Tensile Strength	Tension test
Elastic Modulus	
Residual Stress	On Si wafer
Adhesion	Cross-cut tape test On Si wafer

Table 4 Residual stress and CTE of the synthesized resins

Resin	Mw	Rigidity	Heat reactivity	Residual stress	CTE
A	50,000	○	○	8 MPa	9 ppm/°C
B	36,000	△	△	9 MPa	23 ppm/°C
C	17,000	△	○	10 MPa	23 ppm/°C
D	20,000	×	○	42 MPa	62 ppm/°C

Table 5 Various properties of the resin **A**

Items		Resin **A**
Resin Properties	Alkali-solubility (2.38 wt% TMAHaq)	Good
	Transmittance	i-line non-transparent
Film Properties	Tg	> 400 °C
	CTE	9 ppm/°C
	Thermal Decomposition Temp.	430 °C (5% loss)
	Tensile Strength	130 MPa
	Elastic Modulus	4.4 GPa
	Residual Stress	8 MPa

Table 6 Film properties of ROD-100

Items	ROD-100
Tg	> 300 °C
CTE	18 ppm/°C
Thermal Decomposition Temp.	352 °C (5% loss)
Tensile Strength	90 MPa
Elastic Modulus	5.2 GPa
Residual Stress	13 MPa

equal to that of copper (17 ppm/°C). In addition, the residual stress was also low (13 MPa). However, film properties of ROD-100 got a little worse as a whole compared with those of the resin **A**. That is considered influence of heat resistance of the crosslinking agent to give photosensitivity. Accordingly, we are examining the laser micro fabrication of the resin without crosslinking agents as a next study.

3.3 Chemical resistance

Table 7 indicates results of chemical resistance. ROD-100 showed good chemical resistance to various process chemicals such as Propylene glycol monomethyl ether (PGME)/PGMEA, *N*-Methylpyrrolidone (NMP), Isopropyl alcohol (IPA) and Dimethyl sulfoxide (DMSO).

Table 7 Chemical resistance of ROD-100

Chemicals	Conditions	ROD-100	
		Swelling ratio	Appearance
PGME/ PGMEA	r.t./ 10 min	101%	OK
NMP		100%	OK
IPA		101%	OK
DMSO		101%	OK

3.4 Adhesion

Table 8 exhibits results of adhesion properties by cross-cut tape test. ROD-100 had good adhesion properties to bare silicon wafer and Al substrate with the primer treatment.

Table 8 Adhesion properties of ROD-100

Substrates	ROD-100 (with the primer treatment)
Bare Silicon	100/100
Al	100/100

100/100: No peel was confirmed.

3.5 Lithography performance

Then, lithography performance of ROD-100 was evaluated. Figure 3 shows SEM images of the patterns before and after post curing. As a result, it was confirmed that the size of the pattern was almost same as the size of the mask opening. And, shape change of the patterns after post curing was not observed.

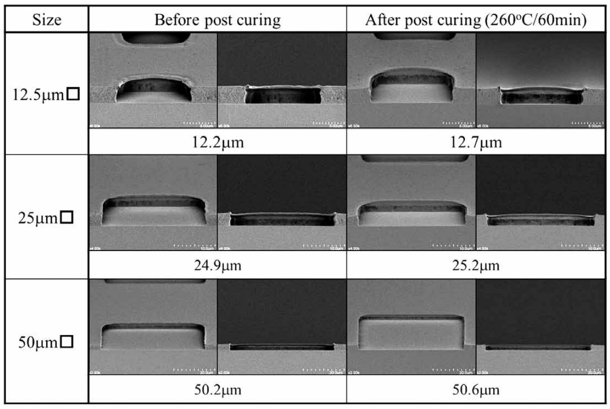


Figure 3 SEM images of the patterns before and after post curing.

3.6 Film thickness change through the process

Figure 4 indicates film thickness change of ROD-100 in each process. When the film thickness after prebaking was 3.0 μm, it got 2.9 μm and 2.3 μm after developing and curing, respectively. As the film thickness change of ROD-100 through the process was c.a. 24%, it was smaller than that of conventional PSPIs (c.a. 40-50%).

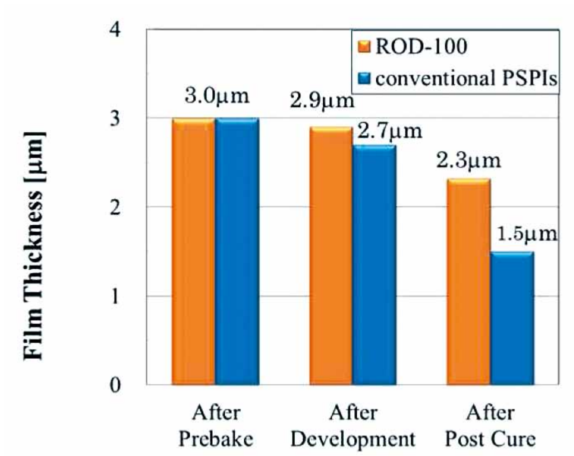


Figure 4 Film thickness change through process.

4 Conclusion

We developed the new negative type photosensitive material with the polynaphthylene resin. The film of the material cured at 260 °C showed low CTE, low residual stress and good heat resistance. And the material exhibited good lithography performance. Thus, we expect application of this material to 3D packaging which requires low CTE and low residual stress by low temperature curing.

Published Conference

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