Negative-tone Photo-definable Polyimide with High Thermal Stability and Thick Film Processability

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Abstract´ High voltage power semiconductor requires higher polyimide insulation properties. We have designed a polyimide with high thermal stability, high light transparency and alkali dissolvable polyimide that is capable of passivating thick layer of polyimide with large topographys. A novel negative-tone photo-definable polyimide was formulated with cross linking reagent that can easily decompose during cure and a photo-initiator that initiates well during lithography. Our novel Negative photo sensitive polyimide, PSPI-1, has a patternable capability up to 16 mm thickness on silicon with 350 mJ /cm^2. PSPI-1 showed higher patternability than of the conventional polyimide. The cured film showed excellent properties as follows: 310 éC glass transition temperature (Tg), 500 éC 5% weight loss temperature, 40% elongation, no short observation during bias-HAST (130 éC. 96%, 100hr, 100V 15/30 mm line&space) and good adhesion to Si and Cu substrates. These results indicated a possibility for this novel PSPI-1 to be applicable for passivating power semiconductor.

Keywords´ Photo-definable polyimide, Thick film, High thermal stability, Passivation layer, Power semiconductor

I. INTRODUCTION

Recently, low loss, high temperature and high voltage power semiconductors are required for high efficient energy use, especially, for electric vehicle application. [1] Polyimide is widely used as a passivation material of semiconductor because of its high thermal and electrical stability; and good adhesion [2]; however, these requirements are becoming more strict in recent years. High voltage power semiconductor requires higher polyimide insulation properties; for in another word, thicker polyimide passivation layer is required because thick insulator shows high voltage resistivity in general. Generally, positive tone photosensitive polyimide (PSPI) is utilized used for the semiconductor processes due to its nature of photolithography function, which reduces the process steps -to reduce the cost of manufacturing. However, since PSPI lack in thermal and electrical properties when compared to non-photosensitive polyimide due to additives for photolithography, choosing PSPI was not favorable. Thick pattern formation is also one of the challenges for PSPI. Due to itslight absorption nature of imide group, PSPI tends to need more light energy during lithography processes.

In this paper, we will introduce and demonstrate the high thermal stability and thick patternability of PSPI-1. This novel PSPI-1 showed thick film patternability up to 16 mm, high thermal stability (Td5=500 éC, Tg=310 éC), excellent adhesion to silicone and copper substrate, and high reliability with high voltage.

II. EXPERIMENT

A. *Polyimide precursor synthesis*

Polyimide precursor resins were synthesized by polyaddition of tetracarboxylic dianhydrides with diamines. The prescribed amount of diamines was poured into a 4 neck flask with a mechanical stirrer, a thermometer and an inlet pipe for nitrogen flow. N-methyl-2-pyrridone (NMP, Mitsubishi Chem.) was added into the 4 neck flask. Under nitrogen flow, the flask was heated to 40 éC. The prescribed amount of tetracarboxylic dianhydrides was added into the flask with NMP. After the mixture in the flask was stirred for 1 hr at 40 éC, the prescribed amount of N,N-dimethylformamide dimethyl acetal was added into the flask and stirred for 2 hr.

After cooling the polyimide precursor solution to room temperature, the solution was poured into the water to precipitate the polyimide precursor. The obtained polyimide precursor precipitate was collected by filtration. The polyimide precursor precipitate was washed by water 3 times. The obtained polymer was dried at 50éC for 72 hours in a convection oven.

B. Preparation of polyimide precursor solution

A Polyimide precursor solution was obtained by following procedure. 10g of polyimide precursor was dissolved by g-butylolactone (GBL) to prepare polyimide precursor solution at concentration of 30¨ 40 wt%. Then, 10~40 wt% crosslinker and 1~10 wt% photoinitiator were added to those solution.

C. Patterning process

The novel polyimide material (see Section II-B) was coated on Si wafer and Cu/Si wafer. After prebake

(120 éC/3min on hot plate), the specimen was exposed by i-line stepper with patterned mask and baked 120 éC/1min as post exposure bake. After development by alkali aqueous developer, the coated material was cured at 380 éC/ 1hr under nitrogen atmosphere. The cured wafer was cut by diamond cutter to observe pattern profile by scanning electron microscope (SEM). Polyimide precursor was transformed to polyimide by the thermal cure process. The cured film was evaluated for various properties (see Section II-D).

D. Measurement of mechanical and thermal properties

Polyimide film of thickness 16 ı m was obtained as in Section II-C without patterning. The coefficient of thermal expansion (CTE) and glass translation temperature (Tg) were measured by thermal mechanical analysis (TMA) equipment (SEIKO, TMA/SS6000) at heating rate 5 éC /min under N_2 flow. Young˘s modulus, elongation and strength of the polyimide film were measured by Universal testing machine (Orientech, TENSILON RTM-100) at rate of 5 mm/min. Mechanical properties measurement were conducted according to JIS K7127 standards. 5% Thermal decomposition temperature was measured by thermogravimetric analysis (TGA) (Shimazu, DTG-60)

E. Thermogravimetric analysis of polymerized cross linker

2g of cross linker and 0.05g of thermal initiator were dissolved in 3g of propylene glycol monomethyl ether acetate in a plastic vial. The solution was poured in aluminum cup and heated by hot plate for curing. The cure condition was 130éC for 10 min and 200 éC for 30 min. Measurement of thermal stability of the resin was performed by TGA under nitrogen gas.

F. UV spectra measurement of polyimide precursors

40 wt% polyimide precursor solutions dissolved in GBL were coated on glass substrate by spin coating, then prebaked (120 éC/3min on hot plate). UV spectra of the films on glasses were measured by UV spectroscopy (Hitachi, U2910).

G. Adhesion strength test

The cured polyimide on wafer was obtained as in Section II-C without patterning. Tape adhesion test of polyimide on Si and Cu was conducted according to ASTM D 3359-87 Method B standards. The criterial is as follows:

5: no peel

4: peel area is less than 5%

3: peel area is over 5%, less than 15%

2: peel area is over 15%, less than 35%

1: peel area is over 35%, less than 65%

0: peel area is over 65%

This test was conducted before and after Pressure Cooker Test (PCT) (ESPEC, EHS-221MD). The condition of PCT was 121 éC, 2atm, 100% RH.

H. Reliability tests-1 (bias-HAST)

Patterned Cu pads and comb electrode were fabricated on 8 inches Si wafer with SiNx surface by sputtering, electroplating and photolithography process. The test element group (TEG) was singulated by blade dicer.

The polyimide precursor solution was coated at 10 ≈m thickness on the TEG substrate as shown in Fig. 1. The dimensions of line, space and height of copper were 15 ≈m, 30 ≈m and 4 ≈m, respectively. Then biased HAST (High Accelerated Stress Test) was carried out at 130 éC for 96 hr with 100 V in 85 %RH. The TEG substrate was fabricated as in Fig. 2.

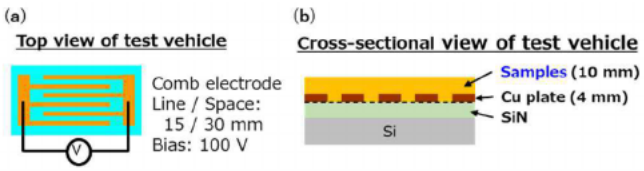

Fig. 1. (a) Top of view of TEG. (b) Cross section of TEG.

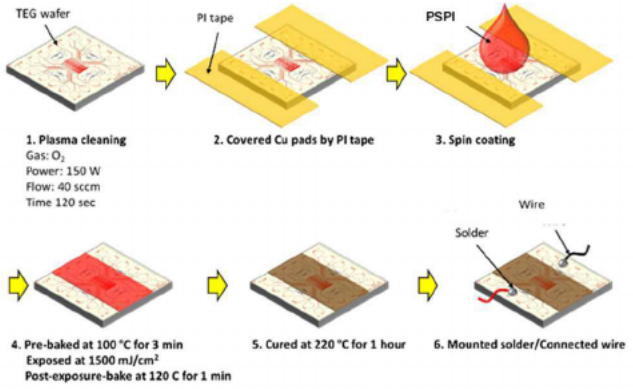

Fig. 2. Procedure of test vehicle fabrication for biased HAST. (a) Top of view of test vehicle. (b) Cross section of test vehicle.

III. Result and Dissussion

A. Design concept of polyimide structure and additive

At first, we focused on thick film patternability with photolithography, which is the biggest challenge for PSPI. In general, polyimide and polyimide precursor absorb lots of i-line (365nm) light derived from imide and amide group of the polymers. We selected polyimide precursor for thick film patterning because of weaker light absorption than polyimide. One of the methods to decrease the light absorption was the aliphatic group introduction to polyimide main chain. However, this method decrease thermal stability. To overcome the trade-off problem, we designed a novel aromatic diamine which had electron withdraw group (EWG) as monomer of polyimide. Mechanisms of light absorption of imide and amide groups are intramolecular charge transfer from nitrogen atom to carbonyl group [3]. By reducing the electron density on

nitrogen atom by EWG, intramolecular charge transfer of polyimide became weaker. We synthesized two different polyimide precursor and derived it from diamine with and without EWG (Fig. 3). Fig.4 shows UV spectra of PI-A and PI-B, transmittance of PI-A was around 60% and PI-B was less than 1%. PI-A is higher transparency at 365nm than PI-B.

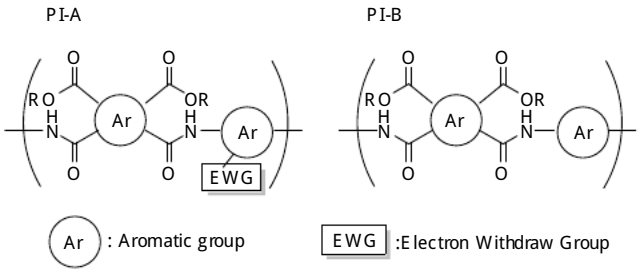

Fig. 3. Modified chemical structure of PI-A and PI-B. PI-A was aromatic polyimide precursor with EWG. PI-B was without EWG.

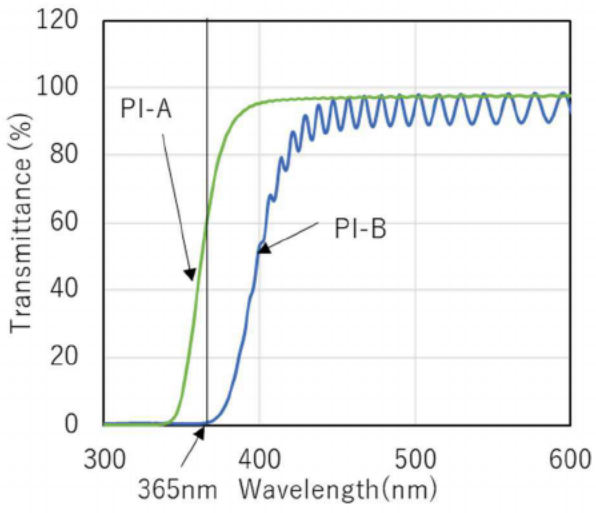

Fig. 4. UV spectra of PI-A and PI-B film (Film thickness=10 mm).

Another challenge of PSPI for power semiconductor was a high thermal stability after cure. Because PSPI includes cross linker and photo initiator for photo-definable property, thermal stability of PSPI is lower than that of polyimide itself. Although the cross linker is essential for photolithography, residue and ash of cross linker in cured film causes lower thermal stability. Our material design strategy is to fully thermal decompose the cross linker during cure. We measured the thermal stability of polymerized cross linkers by TGA, then the samples, which consisted of dipentaerythritol hexaacrylate (DPHA), (well-known cross linker for negative-tone photo definable material) and our new cross linker (CL-A). Fig. 5 shows the result of TGA. Poly(DPHA), that was polymerized resin of DPHA, which had remained 60 wt% of its form even after 380éC (60min) thermal treatment. On the other hand, poly(CL-A) had decomposed after 380éC. This result indicates that CL-A decomposes after cure and doesn˜t have negative effect to cured film for thermal stability.

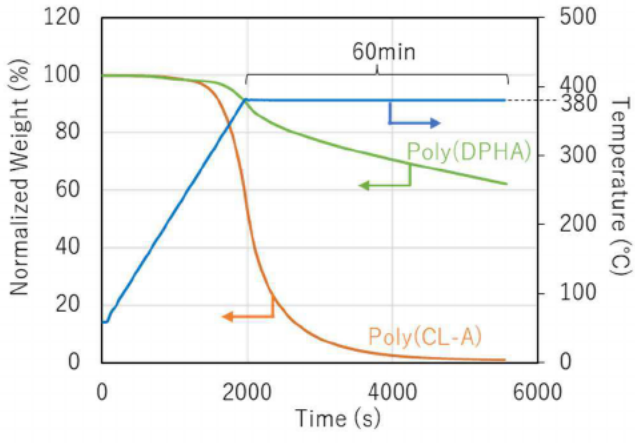

Fig. 5. TGA diagram of poly(DPHA) nad poly(CL-A). Thermal degradation during cure (380éC@60min in N_2) was measured.

B. Patterning, mechanical and thermal properties of new PSPI

We developed novel negative-tone photo-definable polyimide (PSPI-1) made of PI-A with high thermal stability, high light transparency, alkali dissolvable and decomposable CL-A during thermal curing process.

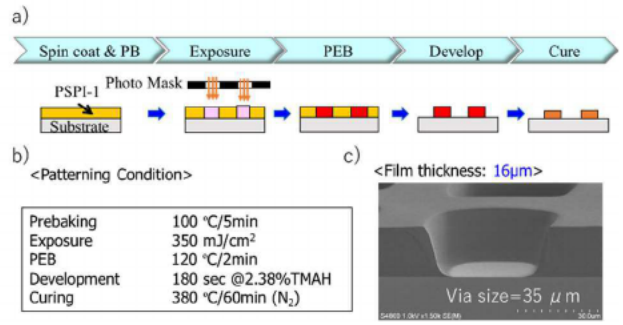

Fig. 6. (a) Process flow of photolithography process using PSPI-1. (b) Process conditions of patterning. (c)) SEM image of 35 ¬m via from cross section view..

PSPI-1 is patternable up to 16 mm thickness on silicon wafer with 350 mJ/cm^2 (Fig. 6) by alkali aqueous developer. Upper limit thickness of conventional PSPI for power semiconductor is usualyy under 10 mm in case of i-line photolithography. PSPI-1 showed thicker patternability than conventional PSPI.

TABLE 1 summarizes thermal, mechanical, and electrical properties of PSPI-1˜s cured film (cured condition was 380 éC/60min). The cured film showed excellent properties as follows: 310 éC glass transition temperature (Tg), 500 éC 5% weight loss temperature, 40% elongation and good adhesion on Si and Cu substrate even after PCT. Dielectric strength was over 450 kV/mm and volume resistivity was over 5 E+16 ohm x cm before and after PCT. Because these properties of PSPI-1 were close to those of PI-A itself, it is assumed that CL-A was decomposed during the cure as expected. Properties of PSPI-1 is expected to be applicable for passivation layer of power semiconductors.

TABLE I. PROPERTIES OF PSPI-1

			PSPI-1
Photo-definable type			Nega. Type
Cure Temp.			380éC
Tg			310 éC
Td5			500 éC
CTE			47 ppm
Young˘s Modules			3.2 GPa
Tensile strength			150 Mpa
Elongation			40 %
Adhesion	Si	PCT 0h	5
		PCT 100h	5
	Cu	PCT 0h	5
		PCT 100h	5
Dielectric Constant			2.91 (1kHz)
Dielectric Loss			0.0022 (1kHz)
Dielectric Strength			475 KV/mm
Volume resistivity			5.68 E+16 W#/m

C. Reliability test results of PSPI-1

We confirmed insulation reliability of PSPI-1 by biased HAST. Usually, voltage of biased HAST is less than 20V and 2~20 mm line and space (Electric field strength is under 1.5 V/mm). However, biased HAST of PSPI-1 was performed at 100V of 15 mm line & 30 mm space TEG (Electric field strength was 3.3 V/mm). As shown in Fig.7, no short and open failure occurred after 100 hours storage at 130 éC with 100 V in 85 %RH. This result indicated that PSPI-1 had enough insulating performance even after a reliability test with high voltage condition.

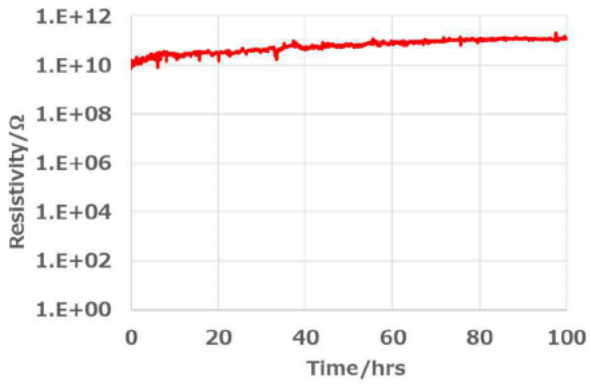

Fig. 7. Resistivity of PSPI-1 during the treatment at a condition of 130 éC, 85 RH% (HAST condtion), and 100 V bias for 100 hrs.

IV. CONCLUSION

Because high voltage power semiconductor requires higher polyimide insulation property,,thicker polyimide passivation layer is required. We have designed a polyimide with high thermal stability, high light transparency and alkali dissolvable polyimide to achieve thick patternability. We also examined high thermal degradable cross linker to be decomposed during cure. Furthermore, this novel negative-tone photo-definable polyimide was formulated by the a new set of novel polyimide, thermal degradable cross linking reagent and photoinitiator. Our novel negative-tone photo-definable polyimide (PSPI-1) has a patternability up to 16 mm thickness on silicon with 350 mJ/cm^{2}and the cured film showed excellent properties as follows: 310 éC Tg, 500 éC 5% weight loss temperature, 40% elongation, no short observation of bias-HAST (130 éC. 96%, 100hr, 100V 15/30 mm line&space) and good adhesion to Si and Cu substrates. These results indicate possibilities for this novel (PSPI-1) to be an applicable passivation material for power semiconductor.

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