Development of High Reliability Insulator with Novel Polymer Containing Flexible Unit

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Due to high market demands in portable electronic devices such as smartphone, tablet PC and wearable electronics, the IC packaging are required to become smaller, thinner, lighter and multiple functionalities. With such complicated and challenged demands, packaging technologies such as WL-CSP, FO-WLP, 2.5D interposer, 3D-TSV, and so on, have been developed and implemented for high volume manufacturing. For these packaging structures, photo-sensitive organic materials used for buffer coating, passivation layers, and insulators for re-distribution are required to exhibit low residual stress to keep higher reliability without any issues such as delamination and cracking. To meet this requirement, we have developed new phenolic resins containing flexible units. Our photo-sensitive insulators containing the new polymer showed low residual stress, good chemical resistance and good packaging reliability. The material design concept and test results are discussed in this paper.

Keyword: Dielectric materials, Photosensitivity, Low residual stress

1. Introduction

With high demands in portable electronic market such as smartphone, tablet PC and wearable electronics, the IC packaging are required to be smaller, thinner, lighter and more functionalities, therefore, the IC packaging become more complicated and challenged. To satisfy such kind of various demands, packaging technologies have become more diversified and widespread such as Wafer Level Chip Size Package (WL-CSP), Fan-Out Wafer Level Package (FO-WLP) and 2.5D interposer [1-5].

For these packaging structures, photo-sensitive organic materials used for buffer coating, passivation layers, and insulators for re-distribution need to satisfy various requirements, such as, low cure temperature, low modulus, low residual stress, high toughness, high resolution, and so on. Low residual stress is an essential requirement to eliminate the delamination or cracking issue for thinner but large die IC packaging and to have higher reliability performance. In industry, currently, some commercial photo-sensitive organic materials like as Polyimides (PI) and Polybenzoxazoles (PBO), were mainly used for buffer coatings, passivation or insulator layers for re-distribution due to its mechanical strength and heat resistance [6-7]. In general, these commercial insulation materials show high modulus and need high temperature curing (>300°C). These can cause high shrinkage stress leading to wafer bow and possible damage to the device [8].

Our current photo-sensitive insulator products contain naphthoquinone diazide (DNQ)
type photo-sensitive compounds for having positive tone lithography performance. And the photo-sensitive insulator is including the phenolic resin as the main polymer, epoxy, the melamine compounds as the cross-linker for enabling low temperature curing (around 200°C) [9-10]. And also our current design contains the low Tg cross-linking rubber particles to release the residual stress. The rubber particles are mainly composed with styrene and butadiene, and have been applied hydrophilic treatment with several monomers to have alkali-solubility and compatibility with the other components [11]. Figure 1 shows the rubber particle TEM picture and cross-linking cartoon symbol. The rubber particle size is around 70 nm and dispersed uniformly in the cured film which can reduce the residual stress effectively. This insulator shows low residual stress due to the combination of the low temperature curing and the stress relaxation.

But, how to design an insulator with low residual stress and high chemical resistance phenolic resin for IC packaging is still a challenge. This paper is to report the design and development concept and to discuss the test data of various properties of low residual stress with high chemical resistance.

2. Design Concept

2.1. Residual stress analysis

Curing and thermal shrinkage stress of our insulator has been tested to confirm the factors of impact total residual stress. The results showed in Figure 3 that the residual stress is proportional to curing shrinkage stress but has minor impact from thermal shrinkage stress. Therefore, the curing shrinkage stress reduction becomes a major action to obtain a low residual stress.

2.2. Improvement of curing shrinkage stress with high chemical resistance

Decreasing cross-linking density to reduce curing shrinkage stress is effective due to the volume shrinkage. However, lower film density cases lower chemical resistance. Therefore, the hydrophobic monomers have been used as a flexible unit for higher chemical resistance. And, if the length of flexible unit is getting longer, it is more effective to release the stress. To verify the effect of these concepts, we studied about polymer molecular weight and the ratio of flexible unit monomer (Figure 4).
3. Experiments

3.1. Shrinkage stress calculation

The shrinkage stress can be calculated by mathematic equation which is separated into curing shrinkage stress ($\sigma_r$) and thermal shrinkage stress ($\sigma_h$). The shrinkage stress also can be expressed by the modulus and strain of product. Therefore, $\sigma_r$ and $\sigma_h$ are calculated by the following equations:

$$\sigma_r = \int_0^{T_{\text{max}}} E(T, \Phi) \cdot \varepsilon(\Phi) d\Phi$$

$$\sigma_h = \alpha \int_0^{T_{RT}} E(T, 0) d\Phi$$

$E(T, \Phi)$ is the elastic modulus at the temperature $T$ and under the reaction rate $\Phi$, $\varepsilon(\Phi)$ is the shrinkage strain at the reaction rate $\Phi$ and $\alpha$ is the coefficient of linear thermal expansion. $\varepsilon(\Phi)$ is calculated from volume shrinkage rate of the cured film. $T_{\text{max}}$ is the maximum cure temperature of 200°C and $T_{RT}$ is the room temperature of 25°C.

3.2. Polymer synthesis

The new phenolic resins were synthesized with p-tert-butoxy styrene (PTBST), monomer which included flexible units, and other key monomers. After polymerization process, the resins were purified with re-precipitation or liquid-liquid separation to remove the remaining monomers. The PTBST in the resins were hydrolyzed to p-hydroxy styrene with HCl or H2SO4. After washing by water and solvent swapping, new phenolic resins containing flexible units were generated. The average molecular weight (Mw) of new phenolic resins was 10k to 40k determined by Gel Permeation Chromatography (GPC) analysis. The co-polymerization monomer ratios were analyzed by Nuclear Magnetic Resonance (NMR).

3.3. Test sample preparation

Table 1 shows the sample preparation process and conditions for lithography performances and physical film properties.

| Process                   | For Lithography | For film properties |
|---------------------------|-----------------|---------------------|
| Film thickness [um]       | 7 um after cure | 15 um after cure    |
| Soft-bake                 | 105°C / 5 min   |                     |
| Exposure (i-line stepper) | 600 mL/cm²      | 1,200 mL/cm²        |
| Development               | 60 sec / 2 times / 2.38 wt% TMAH sol. |
| Rinse                     | 60 sec / DI water |
| Post cure (ramp 3°C / min)| 30°C -> 120°C / 30 min -> 150°C / 30 min -> 200°C / 60 min |

The test samples of photo-sensitive insulator were coated on a Si wafer to targeted thickness for evaluation. And, each test sample was cured at standard curing conditions with several steps of bake, and the final maximum temperature of 200°C.

3.4. Physical properties evaluation

Table 2 shows test methods of physical properties. The physical property of each sample was tested in accordance with Table 2.

| Item                | Test method                                 |
|---------------------|---------------------------------------------|
| Elastic modulus     | Tension test (film thickness: 15 um)        |
| $T_g$               | TMA                                         |
| CTE                 | TMA                                         |
| Solvents            | Dipping in solvent                           |
| Chemical resistance | Flux: WF-6317 (water soluble type, Sanjo Metal Industry Co., Ltd.) |
|                     | Condition: 200°C reflow under N2            |
| Residual stress     | Bonding measurement of Si wafer with 11 um thickness cured film |
| Adhesion to the substrate | Using shear bond tester                      |

3.5. Reliability test

Thermal Cycle Test (TCT) is one of the reliability tests to evaluate the IC packaging fatigue strength. Some issues such as delamination and cracking are caused by stress concentration. To verify the effect of decreasing shrinkage stress, the sample has been prepared and the structure is shown in
4. Results and Discussion

4.1. DOE plan and test sample properties

Table 3 shows the DOE plan for the polymer screening, and the evaluation results of film properties. Sample-1 and sample-2 include same polymers but sample-2 has smaller amount of the cross-linker and test results show that sample-2 has lower shrinkage stress but lower flux resistance. It indicated that loose polymer network is easily swollen by the low molecular weight compound in the flux.

Sample-3 (Polymer-B) has higher monomer ratio with flexible unit and polymer molecular weight than Polymer-A for longer flexible unit. The results show that sample-3 has poor lithography performance due to short phenolic unit length. To achieve higher flexibility and alkali-solubility, the molecular weight and the flexible monomer unit ratio need to be modified.

Sample-4 (Polymer-C) was created and has similar lithography performance and flux resistance as sample-1 but lower amount of the cross-linkers for lower curing shrinkage stress. The test results show that sample-4 exhibited best properties for reliability performance among the evaluation samples.

4.2. Verification of the actual residual stress

A bending test of cured film coated on silicon wafer has been conducted for the residual stress verification. Figure 6 shows the bending test conditions, and Table 4 shows the test results which support that sample-4 has lower residual stress than of sample-1.

4.3. Reliability test

The TCT results are shown in Figure 7. In case of silicon substrates, cracks happened after 300 test cycles (Figure 7 and 8). Crack occurrence rate of Sample-4 was lower than that of Sample-1. Sample-4 which contained Polymer-C with longer flexible unit showed better reliability.
On the other hand, both sample-1 and sample-4 coated on epoxy mold resin passed 600 cycles. The test results also show the CTE mismatch between test sample and substrate is one of the key factors of cracking. The silicon wafer has higher CTE mismatch than epoxy mold resin wafer with cured film (CTE: Si ca. 4ppm/k and epoxy mold resin: ca. 15ppm/k).

Figure 7. TCT results of Sample-1 and Sample-4

![Crack](image)

Figure 8. Optical microscope image of a crack

4.4. Additional properties of Sample-4

4.4.1. Evaluation of the chemical resistance

Table 5 shows the chemical resistance of Sample-4. Films were prepared with the standard conditions as shown in Table 1. We dipped the cured films into the various process chemicals such as organic solvents and photo-resist strippers at 25°C or 40°C for 10 min. The thickness change ratio and the appearance of cured film were checked before and after dipping. The appearance checking is focus on cracking, swelling, wrinkling and discoloring [13]. From the results, Sample-4 shows good chemical resistance with various process chemicals in spite of low cross-linking density. The results support the effect of hydrophobic flexible unit in Polymer-C.

| Chemicals   | Conditions | Sample-4 |
|-------------|------------|----------|
| iME/PGMEA   | 25°C/10min. | OK       |
|             | 40°C/10min. | OK       |
| NMP         | 25°C/10min. | OK       |
|             | 40°C/10min. | OK       |
| PR stripper (TMAH / DMSO) | 25°C/10min. | OK |
|             | 40°C/10min. | OK       |
| IPA         | 25°C/10min. | OK       |
|             | 40°C/10min. | OK       |

Definition of NG: Swelling (thickness change is over 3 %) and/or cracking

4.4.2. Adhesion on various substrates

Additionally, we evaluated the adhesion on various substrates with Sample-4. Figure 9 shows the test method. We compared the adhesion properties of Sample-1 and Sample-4 with a shear bond tester before and after the moisture soak (60°C/60%RH/40hrs.). As shown in Table 6, the adhesion change rate and the water absorption (100%RH/24hrs.) of Sample-4 was lower than that of Sample-1 due to the longer hydrophobic unit in Polymer-C.

![Adhesion test](image)

Figure 9. Adhesion test using Shear bond tester

Table 6. Adhesion properties of Sample-4

|        | Sample-1 | Sample-4 |
|--------|----------|----------|
| Water absorption [%] | 1.9 | 1.4 |
| Adhesion | Initial | After | Δ [%]  | Initial | After | Δ [%]  |
| To Cu   | 27       | 22     | 19      | 31      | 26    | 16      |
| To SiN  | 23       | 21     | 9       | 28      | 27    | 4       |

4.4.3. Lithography performance of Sample-4

The test condition of lithography performance shown in Table 1 was applied for Sample-4 patterning resolution study. Figure 10 shows the Sample-4 SEM images after lithography procedure. Sample-4 could achieve 3μm-C/H (Contact Hole) at 7 μm film thickness.
5. Conclusion
The design concept of low residual stress photo-sensitive insulator with high chemical resistance has been studied and discussed. The curing shrinkage stress is the main contributor to total shrinkage stress which is proportional to residual stress. Photo-sensitive insulator demonstrates higher packaging reliability performance if containing longer flexible unit having low shrinkage stress and high chemical resistance.

References
1. G.J. Jung, “Structure and Process Development of Wafer Level Embedded SiP (System in package) for Mobile Applications”, 2009 11th EPTC, p.191
2. Yoichiro Kurita, “A 3D Stacked Memory Integrated on a Logic Device Using SMAFTI Technology”, 2007 ECTC, p.821
3. S. Yoon, et.al., “Mechanical Characterization of Next Generation eWLB (embedded Wafer Level BGA) Packaging”, ECTC, pp441-446, 2011
4. M. Santarini, “Stacked and Loaded: Xilinx SSI, 28-Gbps I/O Yield Amazing FPGAs”, Xcell Journal, No.74, pp.8-13, 2011
5. M. Murugesan, et.al., “Wafer Thinning, Bonding, and Interconnects Induced Local Strain/Stress in 3D-LSIs with Fine-Pitch High-Density Microbumps and Through-Si Vias”, IEDM, pp.2.3.1-2.3.4, December 2010
6. Y. K. Lee and J. D. Craig, “Polyimide Coatings for Microelectronic Applications”, Polymer Materials for Electronic Applications, ACS Symposium Series, Washington, 1982
7. R. Rubner, H. Ahne, E. Kuhn, and G. Koloddieg, Photogr. Sci. Eng., 23 (1979) 304.
8. J. Yota, et.al., “Variable Frequency Microwave and Furnace Curing of Polybenzoxazole Buffer Layer for GaAs HBT Technology”, IEEE Transactions on Semiconductor Manufacturing, Vol. 20 No.3, 2007
9. D.J. Belton and E. Sullivan, J. Appl. Polym. Sci., 31 (1986) 1309.
10. W. E. Feely, J. C. Imhof, and C. M. Stein, Polym. Eng. Sci., 26 (1986) 1101.
11. Shinichi Iwanaga, Takashi Nishioka, J. I. Electronic Packaging, 9 (2) (2006) 108-112.