Effect of Cross-linker on Photosensitive Polyimide to Achieve Full Imidization and Lower Stress for Good Reliability

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Advanced packaging technology requires low temp. curable and low residual stress material as dielectric layer. Because wafer warpage will be increased with increasing the number of redistribution layers (RDLs) and higher residual stress could induce reliability failure due to cracking and delamination. One method to make residual stress lower is to decrease curing temperature. However, lower warpage by decreasing cure temp. is in a trade-off relation with lower reliability performance due to insufficient imidization ratio of polyimide dielectric layer. To overcome the trade-off relationship, we investigated the effects of number of functional groups and backbone in cross-linker agent. High imidization and low residual stress by curing at 160deg.C have been demonstrated by applying bi-functional cross-linking agent.

Keyword: Polyimide, High imidization, Low stress, Cross-linker, Ultra-low temp cure

1. Introduction
Due to the excellent thermal, mechanical and electrical properties as well as good chemical resistance, polyimide (PI) and poly(benzoxazole) (PBO) have been widely used as stress buffer coatings and redistribution layers (RDL) for packages that have copper re-routing distribution layers to improve the reliability of semiconductor devices [1, 2].

Package structures have been developed to achieve higher performance, downsizing, and cost reduction of electronic devices. Among them, Fan-out packages such as FOWLP (Fan-Out Wafer Level Package) FOPLP (Fan-Out Panel Level Package) are attracting most attention as a new packaging technology [3-5]. Dielectric material used for FOWLPs requires various characteristics such as insulation, low warpage, high reliability, and adhesion strength for metals used as RDL. Particularly in recent years, lower stress has been required to reduce the warpage by increasing the number of RDL and the thinning of chip to prevent failure from cracking and delamination.

Low temperature curing is one method to reduce the warpage. However, lower warpage by lower curing temperature is in a trade-off relation with poor reliability performance due to insufficient imidization ratio.

In order to improve imidization ratio, addition of imidization accelerator such as a thermal acid generator or a thermal base generator can be mentioned, but it is conceivable that these additives remain in the film cure at low temperature. Residual acid and base may corrode Cu wiring and reduce insulation reliability. Therefore, instead of using a new additive, we focused on cross-linker, which is material contained in photosensitive composition and occupies high proportion. Then, cross-linker structure was studied to achieve both high imidization ratio and low stress by curing at 160°C.

2. Experimental
2.1. Materials
Polyamic acid ester as polyimide precursor was synthesized with tetracarboxylic acid dianhydride, diamine and alcohol which is
introduced to side chain of polyimide precursor. Monomers, additives and solvents were used as purchased.

2.2. Evaluation of a model composition
A photosensitive polyamic acid ester varnish was prepared by adding the polymer, photoinitiator, cross-linker, adhesion promoter and other additives to solvent. The varnish was filtered before being spin-coated onto silicon wafers and then prebaked on a hot plate at 100 °C for 2 minutes and 110 °C for 2 minutes. The prebaked wafer was exposed to broadband (g, h, i-line) radiation using a broadband aligner and developed in cyclopentanone by puddle method. The patterned wafer was finally cured at 160 °C for 2 hours under nitrogen atmosphere.

2.3. Calculation of imidization ratio
Imidization ratio calculated by transmission method of FT-IR. Aromatic ring (1500 cm⁻¹) and C−N vibration mode (1370 cm⁻¹) were used to calculate the imidization ratio. The peak of an aromatic ring was reference to normalize C−N peak. The imidization ratio is defined as 0% for prebaked film and 100% for the film cured at 375°C. The imidization ratio was calculated by the following equation,

\[
\text{Imidization ratio (\%)} = \frac{\text{Area of around 1370 cm}^{-1}}{\text{Area of around 1500 cm}^{-1}} \times 100
\]

2.4. Measurement of residual stress
The varnish was coated, soft-baked and blanket exposed onto 6inch silicon wafers and then cured at 160 °C for 2 hours under nitrogen flow. The residual stress of the samples was measured by a thin film stress measurement system.

3. Results and discussion
3.1. Screening of cross-linkers
Various acrylate type cross-linkers and the composition of polyimide precursors were evaluated. Amount of cross-linker was decided so that the number of functional groups were equivalent. Then, we investigated the effect of backbone on the cross-linkers with the most effective functional number.

3.2. Results of Imidization ratio
The imidization ratio was evaluated for a 10μm cured film thickness. As shown in table 1, we found bi-functional type cross-linker showed high imidization ratio even at 160 °C of cure temp. compared to mono-, or multi-functional type. Then, we also found possibility that the imidization ratio can be improved only by selecting the suitable cross-linker, which is essential in the product composition, without using another additive such as a cyclization accelerator.

| Run | Number of functional groups | Imidization ratio (%) |
|-----|-----------------------------|-----------------------|
| 1   | no cross-linker             | 41.5                  |
| 2   | 1                           | 35.8                  |
| 3   | 2                           | 70.3                  |
| 4   | 4                           | 22.9                  |
| 5   | 6                           | 25.6                  |

It is presumed that the imidization ratio was lower by using mono-functional type cross-linker since the polyimide main chain has large side chain made of the cross-linker and reduce flexibility to the polyimide main chain. It is also considered to the composition which no cross-linker is added.

The imidization ratio on Run3 showed relatively higher value than the other experimental runs. It is presumed that bi-functional cross-linker polymerize by itself at exposure step, then the polyacrylate acts as a plasticizer and induce high imidization ratio.

On the other hand, the multi-functional cross-linker didn’t show the acceleration of imidization. It is presumed that cross-linking structure of multi-functional cross-linker was complex and less flexible than bi-functional cross-linker.
Since the bi-functional cross-linker showed higher imidization ratio, we evaluated the effect of the backbone of cross-linker on the imidization ratio. The results are shown in Table 2.

Table 2 Results of imidization ratio of bifunctional group type cross-linker

| Run | Backbone       | Rigidity | Imidization ratio (%) |
|-----|----------------|----------|-----------------------|
| 3   | Aliphatic type | Flexible | 70.3                  |
| 6   | Cyclo-aliphatic type | Rigid | 27.6                  |
| 7   | Heterocyclic type | Rigid | 27.9                  |
| 8   | Bisphenol type | Flexible | 86.0                  |

From the Table 2, the influence of backbone was significant, and the cross-linker with a flexible structure showed higher imidization ratio than rigid type structure.

Based on these results, it was revealed that bifunctional flexible backbone cross-linkers are remarkable imidization promotor.

3.3. Results of residual stress

Next, the effect of the number of functional groups on residual stress was investigated. Then Run 8, which showed higher imidization ratio, was added to evaluation sample. The residual stress was evaluated for a 10μm cured film thickness. The result is shown in Table 3.

Table 3 Results of residual stress

| Run | Number of functional groups | Residual stress (MPa) |
|-----|-----------------------------|----------------------|
| 1   | no cross-linker              | 25.9                 |
| 2   | 1                           | 26.0                 |
| 3   | 2                           | 19.6                 |
| 4   | 4                           | 22.0                 |
| 5   | 6                           | 22.8                 |
| 8   | 2                           | 19.7                 |

As shown in table 3, bi-functional cross-linker was also effective to reduce residual stress compared to mono- or multi-functional cross-linkers. Run 3 and Run 8, which showed high imidization ratio, showed lower stress under 20MPa.

3.4. Discussion

For imidization ratio, the presence of plasticizer accelerates thermal imidization reaction [6]. Therefore, we focused on the Tg of homopolymer made from cross-linker.

As shown in table 4, effective cross-linker on imidization ratio and residual stress showed lower Tg of homopolymer than 100 °C. Then, the homopolymer of cross-linker seems to act as plasticizer at curing process and accelerate thermal imidization. Run 4 also showed Tg below the cure temperature. However, it is presumed that the mobility of the polyimide precursor chain with tetrafunctional cross-linker was more restricted than that with bi-functional cross-linkers because cross-linking density with tetrafunctional cross-linker was higher. The lower imidization ratio with tetrafunctional cross-linker also suggested higher the cross-linking.

Not only imidization but also stress was affected by the number of functional groups of cross-linker. The stress is calculated by the following equation [7].

\[
\sigma = K (\alpha_p - \alpha_s)(T_p - T)E_p \quad (1)
\]

\(\sigma\): residual stress, \(\alpha_p\): CTE for polyimide, \(\alpha_s\): CTE for silicon wafer, \(T_p\): glass transition temperature of polyimide, \(T\): measuring temperature, \(E_p\): Young’s modulus of polyimide, \(K\):constant

The equation indicates that lower Young’s modulus, lower Tg and lower CTE can reduce the stress. Since the bi-functional cross-linker had higher imidization ratio, it is considered that the cross-linking density was lower than that of other cross-linkers. It is presumed that the decrease in crosslink density reduced the young modulus and CTE. Furthermore, Tg of homopolymer made from cross-linkers also affected Tg of polyimide film. For these reasons, the composition with bi-functional
cross-linker showed lower residual stress. Consequently, the adoption of bi-functional cross-linker having a flexible backbone is an effective method, not only for higher imidization ratio but also for residual stress reduction. By achieving high imidization ratio and low stress, it is expected that good reliability can be obtained even by curing at 160 °C.

3. Conclusion
We evaluated the effect of the number of functional groups of cross-linkers. Higher imidization ratio and low stress can be achieved by selecting a suitable bi-functional cross-linker by curing even at 160 °C cure. It seems that bi-functional cross-linkers with flexible backbone act as plasticizer by polymerization during exposure step and that helps acceleration of imidization during curing step. For residual stress, to control cross-linking density and Tg are effective to reduce of residual stress. We can conclude the adoption of bi-functional cross-linker having a flexible backbone is an effective method for both imidization ratio and residual stress.

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