Effect of Sugar Chain Binding Mode on Water-soluble Micropatterning Performance and Physical Characteristics

Toru Amano¹,²*, Makoto Kobayasi¹, and Satoshi Takei¹

¹Department of Mechanical Systems Engineering, Toyama Prefectural University, Imizu, Toyama 939-0398, Japan
²Gunei Chemical Industry, Takasaki, Gunma 370-0032, Japan
*t-amano@gunei-chemical.co.jp

Dextrins commonly known as sugar chains include 1,4- and 1,6-bonded dextrins, which are obtained by enzymatically decomposing starch, and is indigestible dextrin, which is obtained by decomposing starch by an enzymatic reaction and forming 1,2- or 1,3-bonds by acid catalyst treatment. Herein we investigate the water-soluble micropatterning performance of these indigestible dextrins and the change in physical characteristics depending on the structure. The hydroxyl group of each dextrin was modified with a photosensitive group while maintaining water solubility, resulting in a water-soluble photosensitive material. This material was applied onto a silicon wafer using spin coating, exposed with a mask contact exposure device, and then developed with water to evaluate the sensitivity, etching resistance, and coating film strength. The microfabrication evaluation indicated that the performance was sensitive to the binding mode, and it was found that the indigestible dextrin is functional as a water-soluble micropatterning material. Given that this material does not require an organic solvent or a highly toxic strong alkaline developer, it is effective as a low environmental load patterning material.

Keywords: Micropatterning, Photoresist, Sugar chain, Water-soluble material

1. Introduction

Photoresist materials are indispensable in the manufacturing of semiconductor devices and are being miniaturized as electronic devices become more integrated, smaller, more reliable, and faster in signal speed.

In the evolution of electronic devices, a problem has arisen that many resins, solvents, and alkaline developers used in semiconductor manufacturing are treated as waste and disposed of in large quantities.

Conventional photoresist materials are synthesized from fossil raw materials (e.g., acrylic resin and phenol resin), coated with an organic solvent, and developed with a strong alkaline developer or organic solvent. Therefore, it is difficult to reduce the waste that is generated by this process.

In recent years, much attention has been focused on producing water-soluble photoresist materials that can be applied and developed using water.

The primary materials are water-soluble resin, which is a low environmental load patterning material that does not require an organic solvent or a highly toxic strong alkaline developer.

Polyvinyl alcohol, polyacrylamide, and related compounds have been widely studied as water-soluble resins, but since they are produced from fossil raw materials, the environmental load is still significant. [1-8]

A material containing saccharides has been proposed as an alternative water-soluble resist material, but the total environmental load of the process is still substantial because the coating is performed using an organic solvent. [9]

In addition, water-soluble photoresist materials that can be coated and developed with water and are composed of plant-derived and water-soluble sugars (dextrin) have shown promise, but only 1,4- and 1,6-bonds have been studied. An evaluation of only the main general dextrin system was performed, and
the effect of the binding mode is still unknown. [10]
Therefore, we report that the synthesis of water-soluble micropatterning materials using indigestible dextrin formed by 1,2- and 1,3-bonds, along with their exposure sensitivity, etching resistance, coating film strength, and patterning characteristics.

2. Experimental

2.1. Materials

The indigestible dextrins used in this study were made from Roquette (product name: NUTRIOSE) and Matsutani Chemical Industry Co., Ltd. (product name: Fiber Sol 2).

For comparison, dextrin manufactured by Sanei Saccharification Co., Ltd. (product name: NSD500), and NSD500 with the lower molecular weight fractions removed (hereinafter referred to as NSD500Hi) were used.

Gel permeation chromatography (HLC-8320GPC: Tosho) measurements were used to confirm the molecular weight distribution of each raw material and are shown in Fig. 1 and Table 1.

The number average molecular weight ($M_n$) of the NUTRIOSE raw material was 3297 and the weight average molecular weight ($M_w$) was 4567, while Fiber Sol 2 had a $M_n$ of 2783 and a $M_w$ of 4180. In comparison, NSD500 had a $M_n$ of 2454 and a $M_w$ of 11383, while NSD500Hi had a $M_n$ of 7164 and a $M_w$ of 32637.

2.2. Analysis of dextrin binding mode

Indigestible dextrin is a dextrin that contains 1,2- or 1,3-bonds in its structure, as described in the previous section.

The 1,2- and 1,3-bond ratios were analyzed by $^{13}$C NMR spectroscopy (ECZ500R manufactured by JEOL RESONANCE), and the three-dimensional structure was analyzed by Chem3D (ChemOffice 2016 manufactured by PerkinElmer).

2.3. Synthesis of photosensitive polymer

The base polymers (NUTRIOSE, Fiber Sol 2, NSD500, and NSD500Hi) were separately dissolved in N-methylpyrrolidone so that the photosensitive groups (acrylic acid) were 30% denatured with respect to all hydroxyl groups. The system temperature was maintained at 15°C or lower.

Acrylic acid chloride was then added dropwise over a period of two hours.

The solution was then aged for two hours at 15°C or below followed by neutralization with triethylamine. Next, N-methylpyrrolidone and a neutralizing salt were removed and purified, and the remaining material was dissolved in water to obtain a photosensitive material formed from saccharides, as shown in Fig. 2.

The modification to the photosensitive group was confirmed by $^{13}$C NMR and Fourier-transform infrared (FTIR) spectroscopies. As an example, the reaction path of NSD500 is shown in Fig. 2.

Hereafter, the acrylic acid-denatured sugar chains are referred to as NUTRIOSE-A, Fiber Sol 2-A, NSD500-A, and NSD500Hi-A.

![Fig. 1. Comparison of molecular weight distribution of base polymer.](image1)

![Fig. 2. Modification of hydroxyl groups to photosensitive groups.](image2)
2.4. Measurement of exposure sensitivity
The exposure sensitivity of each dextrin with the added photosensitive groups was evaluated.
Omnirad 2959 (manufactured by IGM Resins B.V.) was used as the photosensitizer, and 1 wt%, 2 wt%, or 3 wt% of the photosensitizer was added to aqueous solutions of the acrylic acid-modified base polymers.
The obtained aqueous solutions were applied onto a silicon wafer by spin coating (MS-B100: MIKASA) at 3000 rpm for 30 seconds followed by calcination at 80°C for 60 seconds to volatilize and remove any residual water.
Next, exposure was performed using a mask close contact exposure device (LTCET-500: Lithotec Japan) and a sensitivity confirmation mask (Taiyo-Ink Co.: 5-inch multi-transmission mask), the film thickness was measured, and then the film was developed to determine the residual film ratio, as shown in Fig. 3. By using the above mask, it is possible to easily create a sensitivity curve. NUTRIOSE-A and Fiber Sol 2-A were exposed at 600 mJ/cm², and NSD500Hi-A and NSD500-A were exposed at 1200 mJ/cm².

2.5. Measurement of coating film strength
To determine the effect that the 1,2- and 1,3-bonds of the indigestible dextrin have on the strength of the coating film, the strength was measured by a nanoindenter. The device used was a dynamic ultra micro hardness tester: DUH-211S, manufactured by Shimadzu Corporation.
For the measurements, 3 wt% of a photosensitizer was added to each dextrin, and NUTRIOSE-A and Fiber Sol 2-A were exposed to 300 mJ/cm², and NSD500-A and NSD500Hi-A were exposed to 600 mJ/cm².

2.6. Confirm of microfabrication
Finally, the effect of the 1,2- and 1,3-bonds of the indigestible dextrin on the microfabrication was investigated.
The measurements were conducted with 3 wt% of a photosensitizer added to each dextrin, followed by exposure to 300 ml/cm² for NUTRIOSE-A, Fiber Sol 2-A, and LitesseHF-A, and 600 ml/cm² for NSD500-A and NSD500Hi-A.
The evaluation method is shown in Fig. 4, where a mask close contact exposure device (LTCET-500: Lithotec Japan) and a mask for microfabrication confirmation (Toppan Printing Co., Ltd: TOPPAN-TEST-CHART-NO1-PN) were used.
3. Research and discussion
3.1. Characterization of the indigestible dextrin

The $^{13}$C NMR spectra are shown in Fig. 5 and Table 2.

It was confirmed that indigestible dextrins with 1,2- and 1,3-bonds were not present in generic dextrin. It is speculated that the cause of the high 1,2- and 1,3-bonding ratio in NUTRIOSE is a longer acid catalyst treatment time compared to that of Fiber Sol 2, and the resulting polymer is polymerized. From these results, it was clear that indigestible dextrins contain many branched structures.

The results of the 3D structural analysis by Chem3D are shown in Fig. 6. It can be observed that the molecules are entangled in the case of 1,3-bonds, but there is little entanglement in the other bond types.

From the $^{13}$C NMR spectra and Chem3D, it was found that indigestible dextrins are sugar chains containing many branched structures with some degree of entanglement within the molecules.

Table 2. Results of Measurements of relative binding modes of for various dextrins by determined by $^{13}$C-NMR spectroscopy.

|            | 1,2- | 1,3- | 1,4- | 1,6- |
|------------|------|------|------|------|
| NUTRIOSE   | 5.8% | 28.9%| 44.9%| 20.5%|
| Fiber Sol 2| 2.9% | 19.2%| 60.2%| 17.7%|
| NSD500     | —    | —    | 94.3%| 5.7% |

3.2. Exposure sensitivity evaluation

The results indicate that to obtain a residual film ratio of 80% or more, NSD500-A and NSD500Hi-A must have a photosensitizer concentration of 2 wt% or more and an exposure of at least 900 mJ/cm$^2$ (Fig. 9 and Fig. 10). NUTRIOSE-A and Fiber Sol 2-A were found to achieve a residual film ratio of 80% or more (Fig. 7 and Fig. 8) at a photosensitizer concentration of 2% or more and an exposure of 300 mJ/cm$^2$.

Fig. 5. $^{13}$C-NMR measurement results of various dextrins.

Fig. 6. Three-dimensional structure of the binding mode of sugar chains.

Fig. 7. NUTRIOSE-A sensitivity curve.
The cause of this discrepancy is likely from the difference in the binding modes. Indigestible dextrins with 1,2- and 1,3-bonds are sugar chains with many branched structures and many entangled molecules, and with the addition of a hardening reaction, the molecules become more entangled and insolubilized, leading to an increase in the sensitivity.

3.3. Coating film strength evaluation

The hardness measurements indicated that NSD500-A was soft in terms of the maximum displacement ($h_{\text{max}}$), indentation hardness ($H_d$), and indentation elastic modulus ($E_d$), and no significant difference was found between the other three dextrins (Table 3 and Fig. 11). Indentation elastic modulus ($E_d$), and no significant difference was found between the other three dextrins (Fig. 11 and Table 3).

This phenomenon is explained by the relationship between the exposure sensitivity and the residual film ratio, where a material with a good sensitivity and a high residual film ratio is three-dimensionally crosslinked and contains many polymerized sections.

Typically, the higher the molecular weight, the higher the sensitivity, but NUTRIOSE-A and Fiber Sol 2-A were found to have higher sensitivities than NSD500Hi-A, even though they have much lower molecular weights.

Given that NSD500Hi-A is originally a polymer, a high elastic modulus can be obtained. In addition, NUTRIOSE-A and Fiber Sol 2-A have 1,2- and 1,3-bonds, which results in a multitude of molecular entanglements and therefore an increase in the hardness.

Table 3. Measurement results of hardness and elastic modulus by nano indenter.

|      | $F_{\text{max}}$ (mN) | $H_{\text{max}}$ (μm) | $H_d$ (MPa) | $E_d$ (MPa) |
|------|------------------------|------------------------|-------------|-------------|
| NUTRIOSE-A | 10.04                  | 1.421                  | 267.9       | 3.325E+03   |
| Fiber Sol 2-A | 10.04                 | 1.273                  | 261.9       | 6.502E+03   |
| NSD500-A     | 10.04                  | 2.166                  | 132.9       | 1.245E+03   |
| NSD500Hi-A   | 10.04                  | 1.553                  | 188.2       | 3.679E+03   |
3.4. Microfabrication evaluation

Figure 12-15 shows the microfabricated shapes of NSD500-A, NSD500Hi-A, and Fiber Sol 2-A. During the development as shown in Fig. 4, NUTRIOSE-A peeled off from the silicon wafer, and microfabrication could not be confirmed. In addition, it was observed that while NSD500-A and NSD500Hi-A gave a microfabrication thickness of about 6 µm, Fiber Sol 2-A gave a microfabrication thickness of about 3 µm.

Fiber Sol 2-A has high solubility in water due to its low molecular weight and is highly sensitive given the 1,2- and 1,3-bonds in its structure. These factors provide a good balance between solubility and sensitivity for use in microfabrication.

4. Conclusion

The effectiveness of water-soluble micropatterning materials composed of indigestible dextrins containing 1,2- and 1,3-bonds were investigated. By converting the hydroxyl groups of the indigestible dextrins into a photosensitive group to the extent that water solubility could be maintained, a water-soluble micropatterning material composed of indigestible dextrin was created. The resulting water-soluble micropatterning material has solubility in water and a high sensitivity suitable for microfabrication, in contrast 1,6-bonds.

However, peeling from the silicon wafer was observed in some samples, so improvements in the adhesiveness are necessary.

References

1. H. Morishita, M. Ito, N. Hayashi, and S. Nonogaki, *J. Photopolym. Sci. Technol.*, 7
3.4. Microfabrication evaluation

Figure 12-15 shows the microfabricated shapes of NSD500-A, NSD500Hi-A, and Fiber Sol 2-A. During the development as shown in Fig. 4, NUTRIOSE-A peeled off from the silicon wafer, and microfabrication could not be confirmed. In addition, it was observed that while NSD500-A and NSD500Hi-A gave a microfabrication thickness of about 6 µm, Fiber Sol 2-A gave a microfabrication thickness of about 3 µm. Fiber Sol 2-A has high solubility in water due to its low molecular weight and is highly sensitive given the 1,2- and 1,3-bonds in its structure. These factors provide a good balance between solubility and sensitivity for use in microfabrication.

4. Conclusion

The effectiveness of water-soluble micropatterning materials composed of indigestible dextrins containing 1,2- and 1,3- bonds were investigated. By converting the hydroxyl groups of the indigestible dextrins into a photosensitive group to the extent that water solubility could be maintained, a water-soluble micropatterning material composed of indigestible dextrin was created. The resulting water-soluble micropatterning material has solubility in water and a high sensitivity suitable for microfabrication, in contrast 1,6-bonds. However, peeling from the silicon wafer was observed in some samples, so improvements in the adhesiveness are necessary.

References

1. H. Morishita, M. Ito, N. Hayashi, and S. Nonogaki, J. Photopolym. Sci. Technol., 7 (1994) 59.
2. Q. Lin, T. Steinhausler, L. Simpson, M. Wilder, D. R. Medeiros, and C. G. Willson, Chem. Mater., 9 (1997) 1725.
3. J. M. Havard, M. Yoshida, D. Pasini, N. Vladimirov, J. M. J. Frechet, D.R. Medeiros, K. Patterson, S. Yamada, C. G. Willson, and J. D. Byers, J. Polym. Sci.: Part A: Polymer Chemistry, 37 (1999) 1225.
4. J. M. Havard, S.-Y. Shim, and J. M. J. Frechet, Chem. Mater., 11 (1999) 719.
5. K. Kojima, M. Ito, H. Morishita, and N. Hayashi, Chem. Mater., 10 (1998) 3429.
6. J. Swei and J. B. Talbot, J. Appl. Polym. Sci., 102 (2006) 1637.
7. S.-Y. Shim and J.-M. Kim, Bull. Korean Chem. Soc., 22 (2001) 1120.
8. K. H. Chae, G. J. Sun, J. K. Kang, and T. H. Kim, J. Appl. Polym. Sci., 86 (2002) 1172.
9. Y. Y. Liao and J.-H. Liu, J. Appl. Polym. Sci., 109 (2008) 3849.
10. T. Amano, D. Hirata, Y. Hasegawa, and S. Takei J. Photopolym. Sci. Technol., 33 (2020) 445.
Low Stress and Low Temperature Curable Photosensitive Polyimide

Yu Shoji1*, Keika Hashimoto1, Yutaro Koyama1, Yuki Masuda1, Hitoshi Araki1, and Masao Tomikawa1

1 Department of Electronic & Imaging Materials Res. Labs., Toray Industries Inc., 1-2, Sonoyama 3-Chome, Otsu, Shiga 520-0842, Japan
*yu.shoji.r7@mail.toray

Low stress / low temperature curable photosensitive polyimide (PSPI) with excellent reliability during thermal cycle (TC) has been developed for a quite some time. The effect of residual stress concerning PSPI on copper-PSPI inter-connect structure was examined by Finite Element Method (FEM), and it became evident that the crack has tendency to appear at the top corner between copper and PSPI, where highest stress lay during the cooling process of TC test. Low stress PSPI is one of the candidates to reduce residual stress on copper-PSPI inter-connect structure, and indeed, no crack was found after FEM and TC test. Through a series of tests mentioned above, we came to realize that an introduction of soft segment into polyimide backbone of PSPI is the key factor to create a robust low stress PSPI. In addition of creating a robust low stress / low temperature curable PSPI, further research was conducted to improve the copper compatibility of PSPI through grasping the ways of controlling the oxidation of copper.

Keywords: Photosensitive polyimide, Low stress, Finite element method, Reliability

1. Introduction

Recently, higher density, narrower bump pitch and thinning of 3D Jisso are the trends in the advanced integrated packages. Moreover, in order to implement the trends of advanced integrated packages, an application processor (AP) controlling all functions of mobile devices is believed to be one of the key devices to do so. Thus far, most APs are integrated by Package on Package (PoP) technology, which includes considerable thick substrate for mounting devices [1]. In the recent package trend, Fan-Out Wafer Level Package (FO-WLP) technology became a remarkable package technology, which opened-up a technological window to manufacture extremely thin devices [2]. The FO packages are usually composed of semiconductor die placed in mold resin and redistribution layer (RDL) fabricated on the top of semiconductor die, within mold resin. RDL patterns consist of conductive copper metal and non-conductive insulant materials such as photosensitive polyimide (PSPI) and polybenzoxazole (PSPBO) to insure package reliability. When selecting non-conductive low temperature curable materials, there are several critical requirements to prevent damages to the FO-WLP packages, and one of the requirements is the curing temperature. Selection can easily be fulfilled if robust conventional PSPI and PSPBO, which require high temperature treatment to complete the ring closure reaction; however, FO-WLP require low temperature cure. It is widely known that to complete low temperature ring closure reaction for PBO precursor, introduction of flexible structure in polymer chain worked successfully [3,4]. On the same note, report has indicated that PBO ring closure reaction was accelerated by adding sulfonic acid and photo base generator during low temperature imidization [5,6]. A phenomenon of applying additives to PSPI was also reported by Sasaki [6], which made the development of low temperature curable PSPI for RDL insulator of FO-WLP.

We have developed various type of PSPI materials for several electronic devices such as semiconductor and OLED. A PSPI composed of novel partially esterified poly (amic acid) and
diazonaphthoquinone compound was developed by utilizing photosensitive polymer technologies [7,8]. However, the problem with this polymer technology was that curing temperature over 300 °C necessitated the conversion of poly (amic acid) to polyimide by intermolecular cyclization. For FO-WLP applications, low temperature curable PSPIs were required due to low thermal stability of mold compound and memory device as mentioned before. In addition, copper compatibility and mechanical reliability of PSPI are also important because the FO-WLP technology requires to form copper RDL with PSPI as an insulator.

In this report, the development of low temperature curable PSPI by utilizing a pre-imidized polyimide with low temperature curable cross-linker will be introduced. We have investigated our own development through a series of demonstrative stress simulation of quasi FO-WLP package by changing physical parameters of PSPI by FEM as well as the effect of residual stress of PSPI when utilized for RDL insulators. Furthermore, we have also focused our study to implement copper compatibility to the reliability of PSPI.

2. Experimental

Materials. PI was synthesized by polycondensation of tetracarboxylic dianhydrides with diamines. The proper amount of diamines was placed in a 4-neck flask with a mechanical stirrer, thermometer, and nitrogen inlet. Then, N-methyl-2-pyrridone (NMP) was added to the flask. The flask was heated to 60 °C under nitrogen flow. After diamines have dissolved, the proper amount of tetracarboxylic dianhydrides was added into the diamine solution. The mixture was stirred for an hour at 60 °C, then heated to 180 °C. Polycondensation reaction was carried out at 180 °C for 4 hours. After cooling to room temperature, PI solution was poured into the water to precipitate. The obtained PI was collected by filtration, then dried at 50 °C for 72 hours in a convection oven.

PSPI varnish sample was prepared by following procedure. The dried PI (3.51g), diazonaphthoquinone compound (DNQ, 0.62g), and cross-linker (0.12g) were mixed into 5.75 g of γ-butyrolactone (GBL). The solution was filtered through a 0.2 μm pore poly (tetrafluoroethylene) filter to remove the particles. Chemical structures of DNQ and cross-linkers are shown in Fig. 1.

Pattern formation. The obtained varnish sample was coated on an 8-inch Si wafer by a spin-coater (ACT-8, Tokyo Electron), then soft-baked at 120 °C for 3 min on a hot plate equipped with ACT-8. The film was exposed by an i-line stepper (Nikon, NSR-2205i14) from 200 mJ cm⁻² to 800 mJ cm⁻². After lithographic exposure, the exposed film was developed by 2.38% tetramethylammonium hydroxide aqueous solution (TMAHaq) at 23 °C. Finally, the 5–15 μm PSPI patterned wafer was obtained after cured in a clean oven (CLH-21CD (V)-S, KOYO THERMOSYSTEMS Co., Ltd) at a condition of 180–250 °C.

Measurement. Number- and weight-average molecular weights ($M_n$ and $M_w$) were evaluated by size exclusion chromatography (SEC) on Waters Alliance e2695 equipped with following features: pump, 2489 UV/Vis detector, two polystyrene gel columns of TSK Gel α–2500, and TSK Gel α–4000 (TOSOH) based on a conventional calibration curve using polystyrene standards. N-Methylpyrrolidone (NMP) containing 50 mmol L⁻¹ of LiCl and 50 mmol L⁻¹ of H₃PO₄ (50 °C) was used as a carrier solvent at a flow rate of 0.4 mL min⁻¹. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA6200 thermal analyzer at a heating rate of 10 °C min⁻¹ for thermogravimetry (TG). Seiko EXSTAR 6000 TMA/SS6100 thermal analyzer was also used at a heating rate of 5 °C min⁻¹ for glass transition temperature ($T_g$) and coefficient of thermal expansion (CTE) measurement. Residual stress of cured samples on silicon wafer was evaluated on FLX-3300-T (TOHO) by measuring the curvature radius using a laser at room temperature. Mechanical properties of films such as tensile strength, young’s modulus, and elongation were measured on TENSILON at a speed of 5 mm min⁻¹. To observe the cross-sectional patterns using a scanning electron microscope (SEM) with secondary electrons (FE-SEM S4800, Hitachi Ltd.), the specimens were treated to Pt/Pd sputtering. Film thickness was measured by STM-802 (Lambda Å, SCREEN). The accelerative reliability tests were carried out by treating the film on the substrate with Temperature and Humidity Chamber (PI-2ST, TABAI ESPEC CORP.) as Thermal Humidity...
Storage (THS) test, with a convection oven for High Temperature Storage (HTS) test, and with Thermal Shock Chamber (TSE-11-A, ESPEC CORP.) as Thermal Cycle (TC) test, respectively. Copper migration test was conducted by using copper patterned substrate (Line and Space, 2/2 μm) stored in thermal and humidity chamber with 3.3 V bias. Abaqus 2018.HF3 was applied to carry out stress simulation of FO-WLP model by FEM.

3. Results and discussion
3.1. Stress simulation by FEM

Stress simulation was carried out by Abaqus 2018.HF3 with quasi FO-WLP structure as shown in Fig. 2, and material parameters are summarized in Table 1. Fig. 3 shows that a single layer RDL stress simulation with parameters of Polyimide A during TC test. The highest stress was observed at the top corner between copper and polyimide, especially, during cooling process of TC test. From this data, it is safe to say that crack during TC test may be occurring at high stressed regions.

![Fig. 3. Stress simulation results by FEM during TC test at –55°C and 125°C.](image)

Moreover, the influence of the number of the RDL layer versus occurrence of crack to the package stress simulation was also investigated. When comparing 2 layer structure to 4 layer structure, 4 layer structure showed rather high stress at the top corner between copper and PI (Fig. 4). In order to prove this phenomenon, comparative data between Polyimide A and Polyimide B revealed the answer. These particular results showed Polyimide B with lower modulus than that of Polyimide A showed decreased stress at the corner between copper and PI even in multi layered structure. Therefore, low modulus PI can be considered to effectively

![Fig. 4. Stress simulation results by FEM applying for multi layered model during TC test at –55°C.](image)
suppress or release the package stress, which is expected to enhance the durability for reliability test.

![Diagram of low modulus PI](image)

(A: Alkali soluble group)

Fig. 5. The schematic model of low modulus PI.

### 3.2. Development of photosensitive polyimide with high reliability

According to FEM simulation results, low modulus PI (Polyimide B) is one of the suitable materials for making the stress between copper and PI lower. We designed PI backbone with special soft segment as shown in Fig. 5. The coating material of the obtained PI with soft segment containing DNQ, cross-linker, and other ingredients has low modulus nature (1.7 GPa). Furthermore, low residual stress including alkaline solubility and fine PSPI patterns were successfully obtained even at the thickness range of 5 to 15 µm. Basic properties are summarized in Table 2. Newly developed PSPI shows high thermal stability, mechanical property and high sensitivity in addition to low modulus and stress nature. Fig. 6 shows the SEM images of the fine patterns. The resolution of PSPI is around 5 µm and 10 µm at a 7 µm film thickness, which could be applicable for the metal sputtering.

![Diagram of PSPI](image)

**Table 2. General properties for PSPIs.**

| Properties                      | Measurement Method | Previous Type | Newly Developed |
|---------------------------------|--------------------|---------------|----------------|
| **Curing Condition**            |                    |               |                |
| Tensile strength                | MPa                | 135/135       | 120/120        |
| Elongation                      | %                  | 65/60         | 100/100        |
| Young’s modulus                 | MPa                | 1.7/1.7       | 1.7/1.7        |
| CTE                             | TMA                | 60/58         | 58/58          |
| Residual stress                 | MPa                | 28/29         | 20/20          |
| 5% weight loss temp. T_d         | °C                 | 340           | 340            |
| Volume resistance               | Ω/cm               | >1.0×10^10    | 1.0×10^10      |
| Surface resistance              | Ω/s                | >1.0×10^10    | 1.0×10^10      |
| Photo sensitivity               | mJ/cm²             | 300           | 400            |
| Water Absorption                | % TGA              | 1.0           | 0.8            |

### 3.3. Reliability and copper compatibility of photosensitive polyimide

Reliability tests for the newly developed PSPI with low modulus and low residual stress included TC test, HTS test, and copper migration test. The condition for TC-B test was 1000 cycles at –55 °C to 125 °C. The result of this reliability test was successful, which resulted with no crack.

![Cross-sectional view of via patterns for newly developed PSPI](image)

The other issue regarding reliability is the delamination between copper and PSPI during HTS. Although there is no delamination after cure, delamination and void build-up tend to occur during and after HTS at a condition of 150 °C for 1000 hours. Through a detailed observation by SEM, the interface where delamination and void build-up doesn’t occur between copper and PI, rather it occur between copper and copper oxide layers (Fig. 7 a)). Fig. 7 b) shows the interface by secondary ion mass spectrometry (SIMS) to understand the changes during HTS. Horizontal axis is the depth of copper and PI layers and vertical axis is the detection intensity of various elements. After curing, copper oxide was not formed because curing condition was inert. However, copper oxide was generated after HTS. This result indicates diffusion of copper ion into polyimide and oxidation of copper is taking place during HTS. Therefore, in order to prevent copper oxidation, an introduction of anti-copper oxidant into newly developed PSPI was necessary to suppress copper oxidation. Evidently, when we introduced an anti-copper oxidant into our newly developed PSPI, it successfully suppressed the growth of copper oxide and the diffusion of copper ion.

![Cross-sectional view of the test vehicle, b) SIMS analysis before/after HTS.](image)
Finally, the insulation property of PSPI called copper migration was investigated by bias HAST with 2 μm line and space copper electrode. The result indicates that the reliability of PSPI is quite high because of its ability to keep the resistivity even after THS test at a condition of 130 °C, 85%RH and 3.3 V for 300 hours (Fig. 8).

![Bias: 3.3 V](image)

Fig. 8. The result of copper migration test under bias HAST condition (2 μm line and space copper electrode, 130 °C, 85%RH and 3.3 V for 300 hours).

4. Conclusion

We have investigated the stress effect of polyimide on copper multi-layer structures by FEM simulation. Polyimide designed with soft segment which has low modulus and low residual stress tends to decrease the stress at the corner between copper and PI even in multi layered structure.

The result of PSPI composition based on PI with soft segment when utilized on quasi FO-WLP structure showed promising durability result without crack after TC-B test. In addition, delamination between copper and copper oxide can be successfully suppressed by introducing anti-copper oxidant into PSPI. Moreover, newly developed PSPI showed excellent insulation property investigated by bias HAST using 2 μm line and space copper electrode.

This material is expected to make huge impact and contributions to enhance the reliability of advanced semiconductor packaging.

References

1. M. Takegoshi, N. Suzuki, M. Oze, and T. Ikekuchi, *J. Japan Institute of Electronics Packaging*, 15 (2012) 148.
2. M. Brunbauer, E. Fergut, G. Beer, T. Meyeer, H. Hedler, J. Belonio, E. Nomura, K. Kikuchi, and K. Kobayashi, *Electronic Comp. Technol. Conf. ECTC 2006, 56th* (2006) 5.
3. F. Toyokawa, Y. Shibasaki, and M. Ueda, *Polym. J.*, 37 (2005) 517.
4. K. Iwashita, T. Hattori, S. Ando, F. Toyokawa, and M. Ueda, *J. Photopolym. Sci. Technol.*, 19 (2006) 281.
5. T. Minegishi, S. Ando, F. Toyokawa, and M. Ueda, *J. Photopolym. Sci. Technol.*, 19 (2006) 281.
6. T. Sasaki, *J. Photopolym. Sci. Technol.*, 29 (2016) 380.
7. M. Tomikawa, S. Yoshida, and N. Okamoto, *Polym. Prep. Jpn.*, 56 (2007) 4899.
8. M. Tomikawa, M. Suwa, S. Yoshida, Y. Fujita, R. Okuda, and G. Ohbayashi, *J. Photopolym. Sci. Technol.*, 13 (2000) 357.
Effect of Cross-linker on Photosensitive Polyimide to Achieve Full Imidization and Lower Stress for Good Reliability

Ayaka Azuma*, Satoshi Abe, and Mamoru Sasaki

Technology Development Center, HD MicroSystems, Ltd.
13-1, Higashi-cho 4-chome, Hitachi-shi, Ibaraki 317-8555, Japan
*ayaka.azuma@hdms.co.jp

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 wafer 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, photo-initiator, 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 6 inch 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.

![Cross-linking function](image)

**Fig.1 Structure of 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 bi-functional 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 bi-functional flexible backbone cross-linkers are remarkable imidization promoter.

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.

Table 4 Tg of homopolymer by cross-linkers

| Run | Number of functional groups | Tg of cross-linker homopolymer (°C) |
|-----|-----------------------------|-------------------------------------|
| 1   | no cross-linker             | -                                   |
| 2   | 1                           | 140                                 |
| 3   | 2                           | 23                                  |
| 4   | 4                           | 108                                 |
| 5   | 6                           | >250                                |
| 8   | 2                           | 75                                  |

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].

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

\(\sigma\): residual stress, \(\alpha_p\): CTE for polyimide, \(\alpha\): 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.

References

1. A. Saiki, S. Harada, T. Okubo, K. Mukai, and T. Kimura, J. Electrochem. Soc., 124 (1977) 1619.
2. K. Katoh, Latest Technology of Stress Buffer Material for Semiconductor Application: Nihon Gomu Kyoukai-shi, Vol.58, No.2, p-20-25 (2012)
3. Y. Muno, et al, “FOWLP/FOPLP/Sentan Package Shijoubunseki,” Global Net Corp., (2020).
4. D.-C. Hu, W.-L. Yeh, Y.-H. Chen, R. Tain, “2/2μm Embedded Fine Line Technology for Organic Interposer Applications”, 66th Electronic Comp. Technol. Conf., Las Vegas, NV, 147-152, (2016).
5. S. Brokar, “3D-technology-A System Perspective”, in International 3D-System Integration Conference, 1-14 (2008).
6. Y. Shirai, S. Tokiwa, T. Kawauchi, T. Takeichi, and T. Sasaki. J. Photopolym. Sci. Technol., 25. (2012) 389.
7. M. Ree, C-W. Chu, and M. J. Goldberg. J. Appl. Phys., 75 (1994) 1410.
Purification Method for Achieving Low Trace Metals in Ultra-High Purity Chemicals

Mitsuaki Kobayashi1*, Yukihisa Okada1, Takaaki Shirai1, Osamu Sawajiri1, Robert Gieger2, and Majid Entezarian2

1 3M Japan Innovation Ltd, Separation and Purification Sciences Division, Minami-Hashimoto, Chuo-ku, Sagamihara-shi, Kanagawa 252-5285, Japan
2 3M Purification and Separation Science Division, 400 Research Parkway, Meriden CT, USA 06450

The high purity requirements of materials used in semiconductor manufacturing are being pushed to unprecedented levels as demand for reliability in computer processors over increasingly longer lifetimes continues to rise. The production of these high purity chemicals requires new purification methods and technologies where the metal concentrations of low parts per billion (ppb) were effectively reduced to low parts per trillion (ppt). The new approach discussed in this paper would present a method for dividing the fluid through micro-channels that form tortuous pathways. These micro-channels allow for further dividing and converging of the fluid thereby presenting the metal species to the purifying surfaces throughout the porous matrix. The ion exchange capability was a function of the concentration and the presence of the species in the solution. Two ion exchange chemistries of strong acid and chelating were made into these structures and their purification performances were assessed and compared in terms of removal efficiencies. Furthermore, these two chemistries were evaluated in series to demonstrate the overall synergistic purification capabilities.

Keywords: High purity chemicals, Metal reduction, Ion exchange, Advanced photolithography

1. Introduction

In recent years, the electronic devices have becoming more complex. The line / pattern size in electronic devices is decreasing to levels that impurities play a critical role in the manufacturing, function, and longevity of advanced devices. These impurities are usually classified as cations usually in the form of metal ions, anions of chlorine or hydroxide, or as organic compounds in the form of low to high molecular weight. The removal of these impurities from any fluid that comes in contact with these devices during the manufacturing process is paramount to improving yields and enabling these devices that will shape the future technological advances in medical, diagnostics, communications, artificial intelligence and many more applications. The fluids are Ultra-Pure Water (UPW), etchants, cleaning solutions, Photoresists, developers, coatings, and Chemical Mechanical Planarization (CMP) slurries [1].

There are several purification methods that can be used for purifying fluids. These are evaporation, distillation, affinity purification, filtration, adsorption, fractionation, electrolysis, and ion exchange to just name a few. The focus of this study was the use of ion exchange mechanism. It is stated that the ion exchange process is controlled solely by the diffusion, which is dictated by the materials micro- and macro-structures [2]. One approach that has been utilized to overcome some of the diffusion challenges is to reduce the pore size by utilizing a membrane and grafting an ion exchange on to the membrane surface [3]. Providing high ion exchange capacity does not always results in higher purification outcome. This is more pronounced when approaching very low concentrations for the start. When approaching low ppb metals level and the objective is to achieve low ppt, the diffusion is becoming the rate limiting factor. New approach to improve diffusion is reducing the diffusion path. This is achieved by flowing the fluid through narrower channels. Assuming the ionic species are
the center of the channel, which would be the farthest from the channel walls, the reduction of the channel width directly reduces the diffusion path and reducing the diffusion time. Another approach is to increase the surface contact area between the fluid and the active ion exchange surface, or residence time. Using smaller pore sizes, increasing number of pores, and lengthening of the porous structure would result in increased contact between the fluid and the active surface. Furthermore, dividing the fluid to numerous channels and converging and diverging the stream increases mixing the likelihood of the species coming in contact with active surfaces. The 3MTM Metal Ion Purifiers are building on the above diffusion-controlled parameters by presenting the ion exchange in an immobilized porous micro-channel microstructure. This structure is a porous tubular format, with a similar industry form factor to filtration cartridges. The interaction of the fluid and the microporous immobilized structure is of great interest.

2. Experimental

In this study, two types of 3MTM immobilized ion exchange resin products were evaluated, as shown in Fig. 1. One type is composed of strong acid cation exchange chemistry, identified as “SCP purifier”. The other type is based on a chelating chemistry and is identified as “APP purifier”. SCP and APP represent the model name of two types of 3MTM, Metal Ion Purifier, respectively. The products were cleaned by 3MTM purification technology.

Metals in organic solution were analyzed using Agilent 8900 ICP-QQQ instruments and metals in UPW were analyzed using Agilent 7900 ICP-MS instruments. System was washed with acid several times to obtain a below detection samples before running the tests. Controls were incorporated into the test plan to ensure the elimination of extraneous factors. The sample aliquots were collected by volume intervals processed through the ion exchange blocks.

An effective surface area was measured in use of a Quantachrome (Anton-Parr) Autosorb IQ2-MP. The samples were placed in 9 mm tubes. Outgassing was performed at 60 °C for 14 hours prior to analysis under < 20 mTorr of pressure. The samples were analyzed at liquid nitrogen temperature (~77 K) using ultra high purity nitrogen gas. Void volume was determined using helium. 16 points were taken (adsorption branch) from 0.01 P/Po to 0.3 P/Po. The points between 0.05 P/Po and 0.3 P/Po were fit to the BET equation which defined by S. Brunauer, P.H. Emmett, and E. Teller.

The purifier was initially dry. The dry purifier was so wetted that the purifier works sufficiently. The dry purifier was soaked in an operating fluid. The purifier was mounted in a housing and flushed in minimum of 2 BVs (bed volume) before a purification. In pre-conditioning test, 10-inch cartridge was soaked in UPW with the specific resistance of more than 18.2 MΩcm for 12 hours and flushed by 10 L of UPW. The UPW filtrate was collected in Perfluoroalkoxy alkane (PFA) bottles at 0 L, 6 L, 8 L, and 10 L. The metal concentration was analyzed by Agilent 7900 ICP-MS.

The schematic diagram for performance test was show in Fig. 2. Electronic-grade (EL-grade) 1-Methoxy-2-propanyl acetate (PGMEA) was transferred into an ultra-pure PFA vessel in a pressure tank and pushed through the system by increasing the pressure of the pressure tank. High
purity air was used to pressurized and maintain a constant pressure. The test pressure was adjusted by a compressed air. The clean air was filtered to 0.003 µm rating to ensure no particulate was introduced into the fluid through the line. Prior to starting the test, the 2-inch purifier was installed into the high purity polytetrafluoroethylene (PTFE) housing and sealed to prevent any bypass or leaks. Downstream of the housing, a needle valve was installed for adjusting the flow rate. The 2-inch purifier were soaked in PGEMA for a minimum of 12 hours to ensure the structure is fully wetted by PGMEA and the air in the pores is replaced with the PGMEA in order to maximize the utilization of the ion exchange capacity. The purifier was flushed by 200 mL of PGMEA and was collected in high purity PFA bottles. After completion of the pre-conditioning, the PGMEA in the housing was emptied. The PGMEA spiked standard metal solution the initial 500 mL was discarded, and then subsequent filtrate was collected in high purity PFA bottles. The untreated sample was labeled as “Initial”. All the samples were sealed immediately after filling and opened only when ready for metal analysis by Agilent 8900 ICP-QQQ. More than twenty metal elements were analyzed to assess the effectiveness of each ion exchange chemistry. The metal concentration of spiked PGMEA was around 1 ppb.

3. Results and discussion

3.1. Reaction rate

Generally, the reversible reaction formular of an ion exchange resin is expressed by (1)

\[ R-H + M^+ \rightleftharpoons R-M + H^+ \] (1)

where \( R-H \) and \( R-M \) represents an ion exchange resin bonded with a hydrogen, H, and metal, M, respectively.

The forward reaction velocity \( v_f \) and the backward reaction velocity \( v_b \) are written by (2) and (3), respectively.

\[ v_f = \alpha [R-H][M^+] \] (2)
\[ v_b = \beta [R-M][H^+] \] (3)

where \( \alpha, \beta \) are reaction rate constant for forward and backward reaction, respectively, which strongly related to diffusion velocity in the ion exchange layer.

When fluid with metal ion \( M^+ \) passes through the ion exchange layer with the thickness \( \delta x \) at a liner velocity \( LV \) for \( \delta t \), as shown in Fig. 3. Here \( LV \) is the amount of the fluid which flowed for \( \delta t \) per a unit surface.

A metal variation \( \delta M^+ \) is shown as

\[ \delta t = \frac{\delta x}{LV} \]

Fig. 2. Schematic diagram for the purifier performance test.

Fig. 3. Schematic diagram of fluid flow passing through ion exchange layer.
\[ \delta M^+ = \delta t (v_f - v_h) = \left( \frac{\delta x}{LV} \right) \left( -\alpha [R-H][M^+] + \beta [R-M][H^+] \right) \]  

Initially, an ion exchange resin has initially a hydrogen form \([R-H]\). Then \([R-H] \gg [M^+], [R-M], [H^+]\)

\[ \delta M^+ / [M^+] \approx \left( \frac{\delta x}{LV} \right) \left( -\alpha [R-H] \right) \]  

Metal reduction ratio, \(\delta M^+ / [M^+]\), is proportional to \([R-H]\) and inversely proportional to \(LV\). Also, the metal concentration is a function of the depth, \(x\). Thus the thicker the ion exchange layer, the more is the metal reduction.

3MTM immobilized ion exchange resin technology enabled a purifier with thick ion exchange layer, i.e., depth purifier, as shown in Fig. 4. The depth purifier is more than 100 times as thick as membrane filters. The thick porous micro-channel microstructure enabled to increase. It is seemed that the depth is more effective than membrane filter for trace metal reduction.

While the extreme minimum metal ion concentration \([M^+]_\text{min}\) was obtained at \(\delta M^+ = 0\), that is,

\[ [M^+]_\text{min} = \left( \frac{\beta}{\alpha} \right) \frac{[R-M][H^+]}{[R-H]} \]  

The extreme minimum metal ion concentration \([M^+]_\text{min}\) depends on the metal concentration \([R-M]\). The depth filter may be able to achieve less minimum metal ion concentration \([M^+]_\text{min}\) than a membrane filter, because the depth filter can supply continuously a fresh layer of \([R-H]\) in the downstream. Also it is very important to reduce the initial metal contaminations, \([R-M]\), in ion exchange layer in order to lower the \([M^+]_\text{min}\). 3MTM purification technology enabled to reduce the metal extraction less than 50 ppt in UPW.

3.2. Surface area

The cross section of the 10-inch 3MTM Metal Ion Purifier was shown in Fig. 5. The purifier was tubular with around 15 mm thick and single open end (SOE) where the one end of the tubular was closed by flat end cap and the other end was open through 222-connector. The fluid flowed into from the tubular surface and came out from the connector. The outer surface area of the tube was about 0.05 m². The effective surface area of the purifier was measured by BET to have 32.1 m²/g and 27.1 m²/g for the purifier of the APP and SCP purifiers, respectively. The effective surface area of 10inch APP and SCP purifiers were about 8,000 m² and 7,500 m², respectively, which was extremely larger than the tube surface area. Therefore, it was clarified that the purifiers consisted of porous micro-channel microstructure.

3.3. Pre-conditioning

10-inch SCP was dry. The 10-inch SCP purifier was soaked in UPW for 12 hours and then flushed by UPW at the flow rate of 2 L/min. The other 10-inch
purifier was flushed without soaking. The total trace metal concentration in the filtrate was analyzed by Agilent 7900 ICP-MS, as shown in Fig. 6. The total metal of both SCP purifiers was less than 50 ppt after flushing of 6 L. It was supposed that the low trace metal extraction was owed to increasing contact between the fluid and the active surface by using smaller pore sizes, increasing number of pores, and lengthening of the porous structure. It was clear that 3M™ purification technology could achieve the very high pure SCP purifier with trace metal extraction less than 50 ppt by the increasing contact. The most initial extraction was sodium which seemed to come from the environment and washed out by flushing.

APP purifiers were also flushed in the same manner. The total trace metal was in accordingly with flushing throughput, as shown in Fig. 7. The total metal for the purifier with soaking was less than 50 ppt after flushing of 6 L, while the total metal for the purifier without soaking could not achieve less than 50 ppt even after flushing of 10 L. It is seemed that APP is a little bit slower to be swelled than SCP. It was necessary to swell sufficiently 3M™ Metal Ion Purifier before applying to fluids. It was recommended that the 3M™ Metal Ion Purifier could be swelled sufficiently and flushing.

3.4. Flushing with PGMEA

2-inch purifiers were soaked in PGMEA for 12 hours and then flushed with PGMEA. The trace metal concentration in the filtrate was analyzed by
Agilent 8900 ICP-QQQ. The difference of trace metal concentration in filtrate from the initial PGMEA was shown in Fig. 8. The negative means the reduction from the initial concentration. Any metal extraction from both purifiers of APP and SCP was not observed.

3.5. Metal reduction results

A PGMEA was spiked by metal standard solution so that metal concentration was around 1 ppb. The PGMEA was filtrated by 3M™ Metal Ion Purifier. The results of metal reduction were shown in Fig. 9. The metals less than the quantitative limit of 10 ppt was not shown in Fig. 9. All metals were reduced either to single digit or double digit ppt levels from low ppb or high ppt levels. Both types of the ion exchange were effective in removing all trace metals. It was found that the SCP purifier could remove more sodium than the APP purifier, while the APP purifier could remove more iron than the SCP Purifier. It was supposed that the difference is came from the ion exchange spices of the APP and SCP purifier. The APP and SCP purifier could compensate each other for trace metal reduction.

4. Conclusion

The fixed pore structure in 3M™ Metal Ion Purifier contains high surface area micro channels which reduces the diffusion path allowing for proximity of the metal species to the active sites and
which achieves high cleanness of the active sites. The results of the studies presented in this paper demonstrate that the 3M™ immobilized ion exchange resin technology and purification technology can meet the new requirements for trace metals in high purity chemicals to single digit or low double digit ppt levels from low ppb or high ppt levels.

**Acknowledgement**

The authors would like to acknowledge the contribution of Emiko Toh at corporate research analytical laboratory of 3M Japan Innovation Ltd. for the metal analysis.

**References**

1. Yield Enhancement of International Roadmap for Devices and Systems: (2017)
2. A. Zagorodni, *Ion Exchange Materials*, (2007), Pages 221-241.
3. Y. Tanaka, *Ion Exchange Membranes*, Volume 12 (2015).