Water Permeation Behavior in Polyimide Materials for Polymer Hybrid Bonding

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Abstract
Low-temperature processable polyimide was prepared for 3D stacking polymer hybrid bonding technology. The material has confirmed its reliabilities for semiconductor dielectric film and processabilities such as chemical mechanical polishing. Furthermore, gas permeability of the polyimide film was measured by a differential pressure method. Moreover, the amount of water vapor that can be permeated through insulating layer during the annealing process was estimated. Finally, a series of tests confirmed that water vapor released from the bonded chip.

Key words
Chip-to-wafer, low-temperature process, polyimide, polymer hybrid bonding, gas permeability

I. Introduction
In recent years, hybrid bonding technology, which enables high-density packaging, has been attracting significant attention. This technology already has been utilized in CMOS image sensors and further applications have been considered. One of the advanced applications for this technology is High Bandwidth Memory (HBM) for High-Performance Computing (HPC) [1], [2].

Conventionally, inorganic materials like SiO_2 have been used for the electrical insulating layer, but there are several issues when used for multi-layer chips stacking in HBM manufacturing. The first is the process temperature. Bonding of SiO_2 dielectric layers requires a high temperature of over 300°C, which could cause fatal damage to the memory. The second is warpage. As chips become thinner, the impact of internal stress induced warpage increases, which could lead to bonding failures and alignment errors. Polymer hybrid bonding using organic materials such as polyimides (PI) for the dielectric layer has been developed as a solution to these problems. Since organic materials allow low-temperature process with low elastic modulus and provide the freedom of choosing Coefficient of Thermal Expansion (CTE) to balance out the stress among materials within the package.

Additionally, it is important to consider the impact of outgas on selecting materials for the insulating film in hybrid bonding. According to previous reports, water is generated during the annealing process after SiO_2- SiO_2 bonding, which could create voids. In addition, certain bonding mechanisms for polyimide materials indicated that water could be generated during annealing like SiO_2 [3], [4]. Outgas can occur not only due to chemical reactions of the materials, but outgas can also be generated during cleaning process and alignment for bonding [5]. The behaviors of such generated water include the possibilities of vaporization leading to void formation, diffusion in the material and permeation resulting in external release. These aspects of behaviors have not been fully understood through the study of the materials. However, since organic materials generally have higher gas permeability compared to inorganic materials, especially at high temperatures; therefore, organic materials may have an advantage in excluding water from the film through gas permeation. Identifying and overcoming these property obstacles are important factors when discussing the reliability of devices utilizing polymers for hybrid bonding.

In this study, we investigated the behaviors of water generation during the hybrid bonding process (pre-bonding and annealing), and the gas permeability of the polymer material under high temperature. Based on the measurements taken through the tests, the amount of water vapor that can be released from the chips was estimated. The results were compared with the amount of water generated by chemical reactions and the amount generated by absorption. Based on this comparison, the possibility of sufficient water vapor release was indicated. Additionally, the amount of water vapor released from the bonded chips was measured, and gas permeation was demonstrated.

II. Experiment Section

A. Preparation of polymer

PI was synthesized by reacting tetracarboxylic dianhydrides with diamines in solvent under N_2 gas flow. After the reaction, the reaction mixture was poured into water and washed, and then the precipitation was collected and dried at 50 ºC for 3 days to obtain the PI. The other materials and solvents were obtained commercially and used without modification. PI varnish sample was prepared by following procedure. The dried PI and some additives were mixed into solvent. The solution was filtered through a 0.2 µm pore poly(tetrafluoroethylene) filter to remove the particles.

B. Evaluation of polyimide

Thermal analysis of PI films was performed on a thermal analyzer (EXSTAR 6000 TMA/SS6100, Seiko) at a heating rate of 5 °C/min for glass transition temperature (Tg) and coefficient of thermal expansion (CTE) measurement. Mechanical properties of films such as tensile strength, young's modulus, and elongation were measured on universal tester (TENSILON RTM-100, A&D Manufacturing Company) at a speed of 5 mm/min.
Reliability test on B-HAST was conducted by following process. The polyimide solution was coated at 10 µm thickness on the TEG substrate. The dimensions of line/space and height of copper were 5 µm / 5 µm and 3 µm, respectively. Then, B-HAST was carried out at 130°C in 85 %RH and 5 V bias for 100 hours.

C. General PI-PI bonding test

Bonding strength was evaluated by die shear test. Samples for tests were prepared by the process as shown in Fig. 1. The PI varnish was spin-coated on 200 mm Si wafers by a spin-coater (ACT-8, Tokyo Electoron), and prebaked at 120°C for 3 min on a hot plate, then cured in a clean oven (CLH-21CD (V)-S, KOYO THERMOSYSTEMS) at a condition of 200°C for 60 min under N_2 atmosphere. The chemical mechanical polishing (CMP) process for PI was conducted by the CMP tool (Mirra 200 mm, APPLIED MATERIALS) at a condition of 100 rpm head speed and 2 psi head load. In this process, slurry for resin and hard type pad were used. After CMP, the wafers were singulated into 2.5×2.5 mm chips (top chip) and 12×6 mm chips (bottom chip) respectively using a dicing saw (DAD3350, Disco). The diced PI chips underwent surface activate treatment in Ar atmosphere by plasma etcher (PC-100B+H, Hitachi High-Tech Instruments). Activated PI chips were pre-bonded using a flip-chip bonder (FC3000WS, Toray Engineering) at a condition of 1 MPa load at 250℃ for 3 s. Pre-bonded samples were annealed in a clean oven (CLH-21CD (V)-S, KOYO THERMOSYSTEMS) at a condition of 250°C for 60 min under N_2 atmosphere. Then, die shear test was conducted by bond tester (Dage Series 4000, Nordson Advanced Technology).

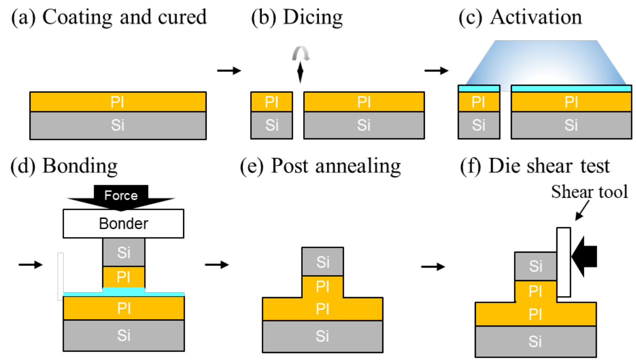


Fig.1 Process of general PI-PI bonding test.

D. Measurement of gas permeability

Gas and water vapor permeation analysis of PI film was conducted as shown in Fig. 2. The PI varnish was spin-coated on 200 mm Si wafers by a spin-coater (ACT-8, Tokyo Electoron), and prebaked at 120°C for 10 min on a hot plate, then cured in a clean oven (CLH-21CD (V)-S, KOYO THERMOSYSTEMS) at a condition of 200°C for 60 min under N_2 atmosphere. PI film with a thickness of 30 µm was obtained by peeling off in 47% hydrofluoric acid. Using the film sample, the permeation rates of nitrogen gas and water vapor in a humid atmosphere from room temperature to 150°C were measured with a differential pressure method. The detail condition shown in Table I.

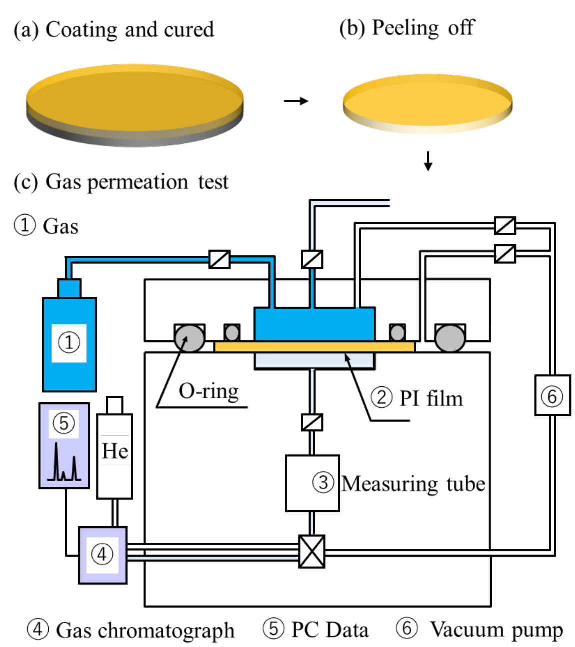


Fig.2 Process of gas permeation test.

Table I. The detail condition of gas permeation test.

Equipment	Gas and Water Vapor Permeation Analysis System (GTR-30XA, GTR TEC)
Temperature (Relative Humidity)	25°C (30%RH), 70°C (5%RH), 110°C (5%RH), 150°C (5%RH)
Test gas	Nitrogen gas and water vapor
Gas permeation area	15.2 cm²
Film thickness	30.2 μm

E. Out gas measurement

Out gas measurement of PI film was carried out by Temperature Programmed Desorption Mass Spectrometry (TPD-MS). Outgas was identified by Thermal Desorption Gas Chromatography / Mass Spectrometry (GC/MS) method. Thermal desorption apparatus (ACEM9300, Dynatherm) was used for this test. Table II presents the detail condition.

Table. II The detail condition of TPD-MS.

Equipment	GC/MS (QP2010, Shimadzu) with heating apparatus (TRC)
Data processing	Thermal analysis data processing system (THADAP-TG, Toray Research Center)
Sample area	4.3 cm² (6 chips = 3 bonded chips)
Atmosphere	He flow (50 mL/min)

III. Results and discussion

A. polymer for low temperature bonding process

For this experiment, polyimide material PI-1 which is designed for hybrid bonding in low-temperature processes was prepared. The film properties were measured and general bonding test using PI-1 was conducted. The evaluation results are shown in Table III.

Table. III General properties of PI-1

Properties		PI-1
Curing condition	°C/min	200
Tensile strength	MPa	140
Elongation	%	68
Young's modulus	GPa	3.2
Tg	°C	283
5% weight loss temp.	°C	440
Reliability test	-	Pass
CMP rate	nm/min	>500
Die shear strength	MPa	>25

It was confirmed that PI-1 has fine tensile strength, heat resistance, and elongation. Regarding reliability test, it was found that resistivity could be maintained during a B-HAST test with a voltage of 5 V for 100 hours on a 5/5 μm L/S. This result indicated that PI-1 have enough insulating performance as dielectric layers for hybrid bonding even after the reliability test. Also, for applications, such as memory devices, which are sensitive to thermal treatment during the bonding process, it is preferred to conduct the bonding process at a low temperature. Additionally, considering the takt time, the CMP rate is also important. For the processability of PI-1, die shear strength of over 25 MPa can be achieved with a bonding pressure of 1 MPa in processes at low-temperature of below 250°C. Moreover, CMP rate of over 500 nm/min, that is enough high for high throughput, was demonstrated. Thus, good mechanical properties, insulation reliability, CMP processability, and low-temperature bonding capability of PI-1 as a semiconductor insulating film were verified.

B. Gas and Water Vapor Permeation Analysis

1) Results of tests

For PI-1 film, gas permeability of water vapor and nitrogen gas under humid conditions was measured with a differential pressure method. The measurement was performed at 25°C, 70°C, 110°C, and 150°C. Table IV shows nitrogen gas transmission rate (NGTR) and nitrogen gas permeability coefficient (P_N). Table V shows water vapor transmission rate (WVTR) and water vapor permeability (P_W).

Table. IV Nitrogen gas permeability measurements

Temperature (T)	Relative Humidity	NGTR	P_N
°C	%RH	cm^3 /m^2・day・atm	cm^3・cm /cm^2・s・cmHg
25	30	10	4.6E-13
70	5	52	2.4E-12
110	5	210	9.7E-12
150	5	660	3.0E-11

Table. V Water vapor permeability measurements

Temperature (T)	Relative Humidity	WVTR	P_W
°C	%RH	cm^3 /m^2・day・atm	cm^3・cm /cm^2・s・cmHg
25	30	1.5	9.4E-9
70	5	4.5	1.7E-8
110	5	35	2.8E-8
150	5	150	3.7E-8

It was observed that NGTR and WVTR tend to increase with rising temperatures. Additionally, P_N and P_W can be approximated by an Arrhenius plot with respect to temperature (1), [6].

$$P = P_0 e^{-\frac{E_P}{RT}} \ (1)$$

By fitting the measured results, good correlation coefficient was confirmed. From the approximation equation, P_N and P_W at process temperatures above 200°C were estimated. Additionally, the activation energies (E_P) were calculated from the approximation equations. The results are shown in Fig. 3 and Fig. 4.

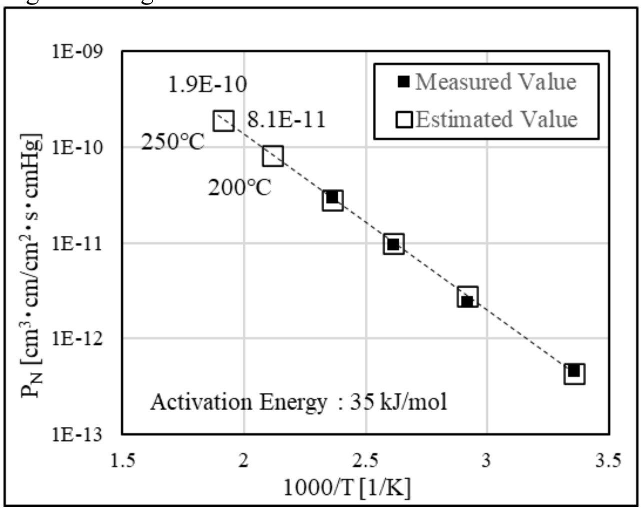


Fig.3 P_N at each temperature.

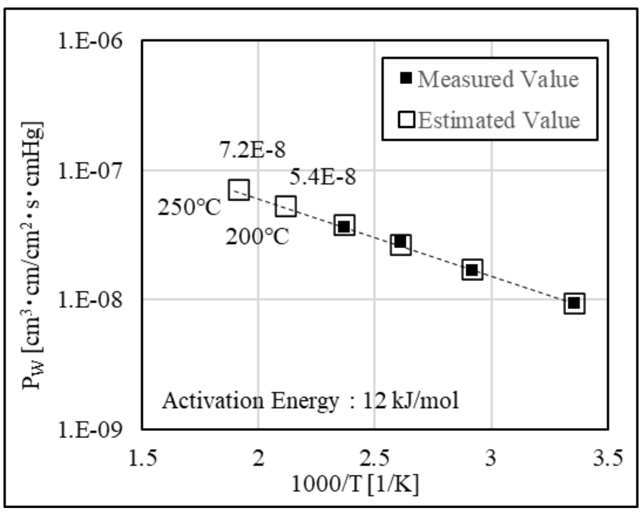


Fig.4 P_W at each temperature.

A higher permeability coefficient for water vapor compared to nitrogen gas was observed. Since the gas permeability coefficient can be expressed as the multiplicative product of the diffusion coefficient and the solubility coefficient, this is considered to be influenced by the differences in the size of gas molecules and their solubility in the insulating membrane. Additionally, the activation energy for water vapor showed a smaller value. This is presumed to be because of increased diffusivity and decreased solubility of water vapor with rising temperatures, which counteract each other, resulting in a lower activation energy.

2) Estimation of water passing through the chip

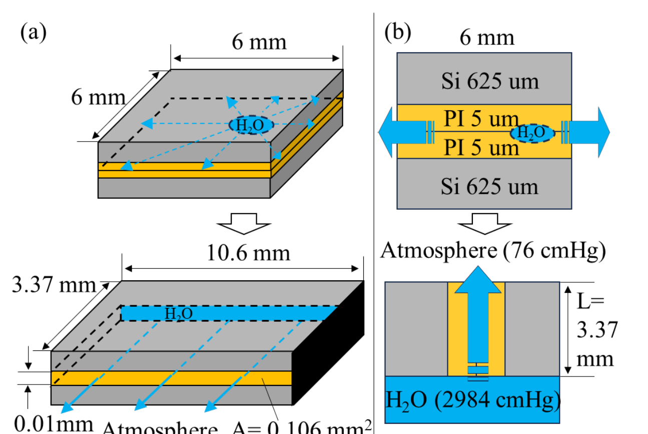
Using the obtained P_W at 250°C and (2), the amount of water vapor that can be released from the 6 mm x 6 mm bonded chip during the post-annealing process in hybrid bonding was calculated.

$$P = \frac{Q \times L}{A \times t \times \Delta p} \ (2)$$

Considering the case where bonded chips which were coated with 5 um PI-1 underwent post-annealing process at 250°C for 1 hour, it was estimated that up to 1.90 µg of H_2O could permeate and be released by following calculation. Here, it was assumed that all the generated H_2O vaporizes in the membrane and permeates due to the pressure difference between the vapor pressure of water at 250°C and atmospheric pressure [7]. The P_W of PI-1 at 250°C was set to 7.2E-8 cm^3 cm/cm^2 s cmHg, and the permeation length and permeation area were taken as the average values of the distance from any point inside the chip to the chip periphery and the cross-sectional area to permeation length, respectively (Table VI and Fig. 5).

Table. VI Calculation conditions and results

Chip size	mm	6 x 6
PI thickness	µm	5
Permeation length (L)	cm	0.337
Permeation area (A)	cm^2	1.06E-3
Permeation time (t)	s	3,600
Pressure difference (Δp)	cmHg	2,908
Water vapor permeability (P)	cm^3 cm /cm^2 s cmHg	7.2E-8
Estimated water permeation volume (Q)	cm^3	2.37E-03
	µg	1.90



$$A \approx \pi L \times 0.01 = 0.106\ [\mathrm{mm}^2] \quad L \approx \frac{12}{\pi}\int_0^{\frac{1}{4}\pi} \frac{d\theta}{\cos\theta} = 3.37\ [\mathrm{mm}]$$

Fig. 5. Image of assumed sample conditions. (a) 3D image, (b) Cross sectional image.

Next, the estimated water permeation volume was compared with the amount of water generated from chemical reactions and processes to assess the feasibility of permeation. The amount of H_2O generated by chemical reactions was calculated assuming an activation layer of 10 nm created by plasma treatment, where all imide bonds in the activation layer are cleaved and hydrophilized, and then underwent intermolecular imidization during the post-annealing process. It was found that the amount of H_2O generated by chemical reactions at the bonding interface is significantly lower than the amount of H_2O that can be released through gas permeation.
Additionally, for water derived from processes such as cleaning and water alignment, it was assumed that all process-induced water was absorbed into the membrane and vaporized during the annealing process. In this calculation, the water absorption rate of the PI material was assumed to be 1%. As a result, even if all the moisture in the membrane vaporizes, it is calculated that approximately 44% can permeate and be released. It is considered that the entire amount can be released with about 140 min of annealing.
Furthermore, the actual measured amount of H_2O released from a PI-1 film cured at 200°C and annealed at 250°C for 1 hour was shown as a reference. The measurement was conducted using TPD-MS. Regarding the actual measured values, it is calculated that approximately 100% can permeate and be released. Considering the actual annealing process, gas permeation during temperature ramp-up and ramp-down can also be included as a margin. Hence, it is believed that almost all the moisture can permeate and be released.
Thus, calculations confirmed that the moisture generated from the insulating film is sufficiently passed through from the chip under appropriate anneal process condition. Table VII exhibits the results of comparison.

Table. VII results of comparison.

H_2O source	Amount of H_2O*1	Permeation ability*2
Chemical reaction (estimated value)	1.51E-3 μg	> x1,000
Water absorption (estimated value)	4.32 μg	44%
PI-1 (measured value)	1.87 μg	102%

*1 Conversion value from 2 chips (36 mm^2 x 2) with PI of 5 μm thickness.
*2 Comparison to estimated water permeation volume (1.90 μg) in Table VI.

However, the calculations were based on the assumption that the generated H_2O vaporizes within the membrane and then permeates through. It is considered that in fact the H_2O diffuses through the membrane without vaporizing, and partially released.
Besides, it is predicted that the polymer membrane exhibits orientational characteristic, resulting in differences in permeability coefficients depending on the direction of permeation.
Also, this is a calculated value for water vapor, and it is important to note that the pressure conditions differ for voids caused by air entrapment during bonding because the permeability of nitrogen in air is approximately two orders of magnitude lower compared to water vapor.
Therefore, this result should be used as a guideline when considering materials and process, and the absence of voids should be verified through actual test.

C. Demonstration of water vapor permeation

1) Process
Finally, it was demonstrated that water vapor is permeated from the bonded chip. Following the flow in Fig. 6, the bonded chip was obtained. For the bonded samples, TPD-MS measurements were conducted under a helium atmosphere, heating from room temperature to 250°C.

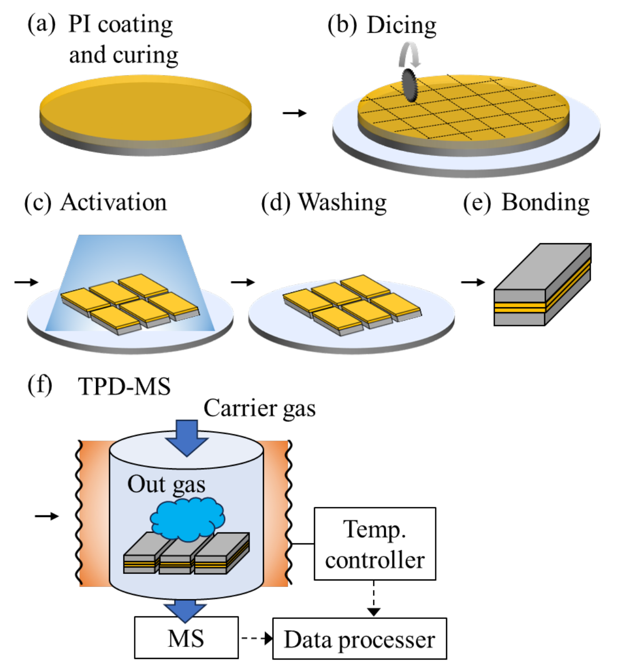


Fig. 6 Process flow of TPD-MS analysis (a) Coated with 5 μm PI-1 and cured at 200°C for 1 hour in N_2, (b) Singulated into 12 mm x 6 mm chips, (c) Under Ar for 20 s, (d) DIW rinse and air blow, (e) Bonded at 4 MPa/250°C/5s, (f) Heated up to 250°C at heating rate of 10°C/min.

2) Results of TPD-MS
Table VIII demonstrates the results of TPD-MS. Also, the C-SAM images of the bonded chip, annealed at 250°C for 1 hour, are shown in Fig 7.

Table. VIII Result of TPD-MS

m/z [a]	Identification	Detected amount (μg/cm^2) [b]
18	H_2O	1.74
28	N_2, etc.	0.00
32	O_2, etc.	0.00
33-	other gas	0.05 *

[a] m:mass number, z:ion charge
[b] the weight of each gas (μg) / sample area (cm^2)
* Conversion value using 1-Butene as standard gas

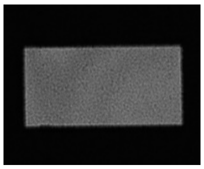


Fig. 7 C-SAM image of bonded chips after annealed (observed by FineSAT, Hitachi Power Solutions).

It was confirmed that approximately 1.74 μg/cm2 of moisture was permeated from the bonded chips. Although it is unclear whether all gases were released, it was confirmed that there is no significant difference from the amount generated from the single film as listed in Table VIII.
Moreover, C-SAM images show no voids between the bonded chips.
Thus, water vapor permeation of PI film was demonstrated.

D. Future challenges

We plan to compare the water permeability of the polymer obtained in this study with that of inorganic materials such as SiO_2 although it is difficult to compare directly because the gas permeability of inorganic materials is expected to vary significantly depending on the condition in the deposition process.

IV. Conclusion

A polyimide material, PI-1, designed for polymer hybrid bonding in low-temperature processes was prepared, and its reliability and processability as a semiconductor insulating film were confirmed. Gas permeability of PI-1 was measured up to 150°C. The water vapor permeability was higher than the nitrogen permeability, and the permeability tended to increase with increasing temperature. The gas permeability at temperatures above 200°C was calculated by Arrhenius plot of the permeability coefficient against temperature. We estimated the amount of water that can be released from the chip in the expected HB process according to the calculated number.
It was confirmed that H_2O generated by the chemical reaction can be sufficiently released, and the process-induced water is also expected to be permeated by adjusting the conditions. Additionally, comparing the actual measured values of water vapor generated by heating PI-1, the calculated results showed that nearly 100% of the moisture could be removed under the assumed conditions. The amount of moisture generated from the bonded chip was measured using TPD-MS. It was confirmed that H_2O can be eliminated from the bonded chip without significant difference from the calculated results. Moreover, no void was observed from C-SAM image of actual bonded chips.
The generation of H_2O due to the dehydration reaction during the post-annealing process occurs in both inorganic and organic materials. Demonstrating that water can penetrate PI films to the outside of the chip without forming voids is an important result for discussing the reliability of semiconductor devices manufactured by HB. The gas permeability might be one of the advantages of organic materials.

Acknowledgment

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