

# Extreme Temporary Coatings and Adhesives for High-Thermal, Low-Pressure, and Low-Stress 3D-Processing

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## Abstract

Although several materials are commercially available as temporary adhesives in 3-D packaging, few candidates satisfy processes of elevated temperature and extreme vacuum. Whether these include thermoplastic or thermosetting polymers, success is met by their being processed in a manner that meets the customer's low vacuum conditions. This paper presents data on several products and methods of modeling a customer's process. Low-cost alternatives will be presented which may be easily integrated, provided that a customer's process can be tuned to accept such materials. Low-cost temporary support materials allow grinding and polishing to <20um while also protecting front side devices from backside processing to include through silicon vias (TSVs) and the associated cleans and metallization steps. Temporary adhesives must sustain thermal resistance to 250C, vacuum conditions of 10-6 Torr, and shear forces of grinding processes. These properties are required for via etch, CVD processing (e.g. oxide deposition), and chemical use during cleaning. These efforts are aimed at simplifying the overall process, aligning chemistry, and many times, eliminating the need for complicated cleans. By tailoring a customer's process to accept a lower-cost adhesive, new ways of simple and rapid cleaning or even detergent washable systems may be integrated. Using these approaches, a safer working environment, or green factory, may be achieved while reducing the use of organic solvents and eliminating waste. Several options will be presented for using low-cost adhesives in thinning and backside processing towards increasing throughput and reducing cost. Examples will include semiconductor wafer and die thinning and at least one non-semiconductor thin substrate practice.

Key words: adhesive, thinning, thermal resistance

## I. INTRODUCTION

Wafer thinning and backside processing are an integral part of 3D packaging. All current technologies involve a temporary adhesive and a carrier to support a thin substrate to below 20 um. Of the common wafer support practices, an adhesive bonded carrier is the most reliable, able to support thin substrates and exhibit the chemical and thermal resistance necessary for backside work (Table 1).

Table 1. Options and their properties for thin wafer support.

Thin Wafer Handling	Thickness (um)	Chem & Therm Resistant	Single Wafer or Batch	Backside Process Support
Tape	>50	No	Both	No
Vacuum Chuck	>50	No	Single	No
Adhesive Bonded Carrier	<25	Yes	Both	Yes

The use of carriers offers good surface planarity, measured as a low TTV, and are believed to reduce both internal stress and wafer bow during grinding [1-4]. Liquid spin-on forms of adhesives offer easy control of TTV. When the coating is applied to smooth (native) and patterned wafers, acceptable thinning uniformity may be achieved if the TTV is  $\leq 0.5\%$  [5-5]. Once thinned, the adhesive continues to hold the substrate

in place through backside processing, a series of steps that may include TSVs, metallization, and extend to dicing. Although a customer's backside processing choices may vary, a common feature to the use of any temporary adhesive with a carrier is includes two active stages, namely, bonding and de-bonding (Fig. 1).

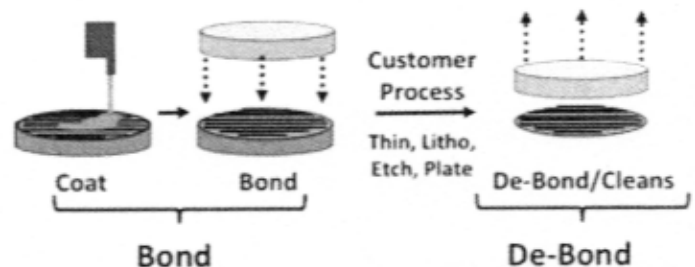


Fig. 1. Two active stages to the use of any temporary adhesive and carrier, bonding and de-bonding. Cleaning is included in the de-bonding practice.

At the time of this publication, there are no less than a half dozen temporary adhesives used in the marketplace for thin semiconductor wafer handling. All of these practices are differentiated by their chemical family. These products include the following, their market capture in decreasing order: a) rubber/olefinic [7-8], b) acrylic [9], c) silicone [10], d) polyimide, and e) rosin-urethane [11]. It is curious to note that although these chemistries vary, their methods of application and bonding are similar, namely, the material is coated onto the wafer, cured, and bonded to the carrier (Fig. 1). The main

variance in performance and complexity is in their de-bonding (Fig. 2).

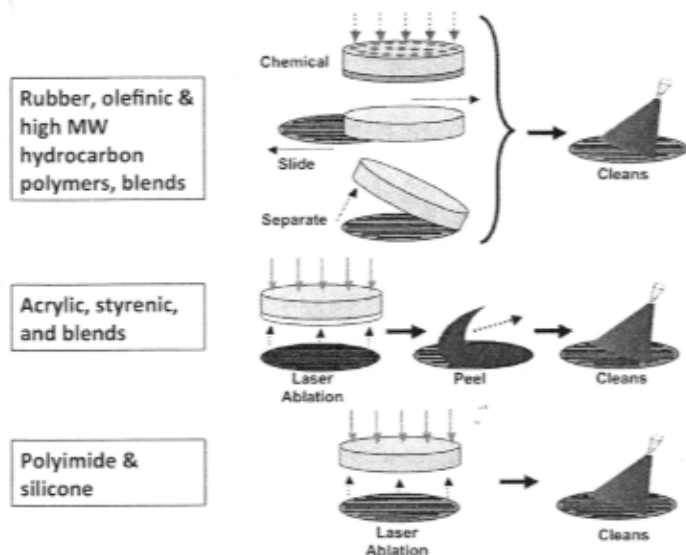


Fig. 2. Leading temporary adhesives commercially available at the time of publication. These materials vary according to their de-bond performance and complexity.

De-bonding of the rubber/olefinic adhesive is offered by three choices, including chemical dissolution through a perforated carrier, thermal slide, and separation of the carrier by the use of a reduced adhesion layer to an inner region of the carrier that has been previously prepared and masked. An acrylic-based temporary adhesive requires laser ablative attack of the interface between the carrier and adhesive and once removed, the remaining adhesive layer is peeled away from the thinned product wafer. Other options include the use of polyimide and silicone adhesives, both of these technologies require the use of laser ablation to facilitate removal. All of these technologies irrespective of their de-bonding, must incorporate a final cleaning step to remove adhesive residue from the product wafer.

As summarized here, the temporary adhesives that lead the effort for thin wafer handling in 3D processing use a carrier wafer, exhibit similar application and cure, however, they vary widely in performance and complexity for de-bonding. These materials may represent acceptable performance standards for research in the area of 3D-processing, yet are likely not to meet HVM's strict requirements for quality and cost. Several options are presented here for temporary coatings and adhesives to achieve thermal, outgas, and stress requirements.

#### A. Thermal Resistance

One of the most unique commercial polymer products available for solving thermal resistance challenges is polybenzimidazole (PBI) [12]. The aromatic bi-benzimidazole structure provides superior chemical and thermal resistance due to the strength of its internal molecular bonds (Fig. 3).

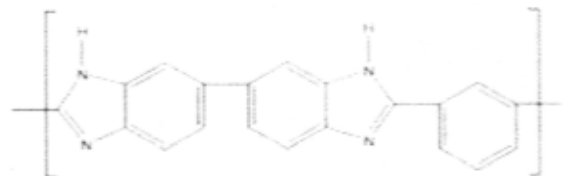


Fig. 3. Chemical structure of PBI polymer.

PBI polymer is represented at the top of the maximum temperature index of the polymer performance triangle, exceeding the thermal resistance properties of unfilled engineering polymers used for solving industry's most complex challenges (Fig. 4).

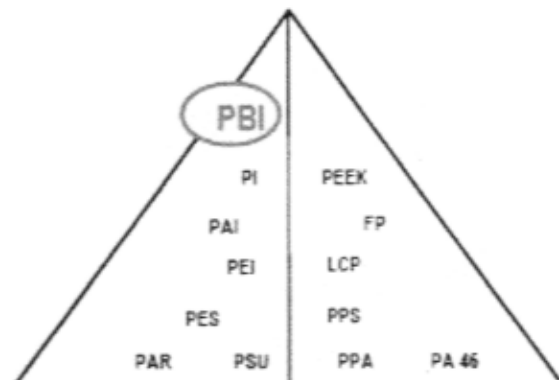


Fig. 4. Top of performance triangle, products of  $>150\text{ }^{\circ}\text{C}$  temperature index, amorphous (left) and partial crystalline (right).

PBI coatings are used to protect underlying metal from aggressive conditions from the combination of heat, moisture, and chemicals. A thin coating on high-carbon or stainless steel increases the wear property of the substrate. PBI has also been proven useful in high vacuum plasma chambers to increase the life of seals, gaskets, and other wearable components. PBI materials are especially resistant to oxidative and thermal aggressive conditions found in plasma equipment. Coatings of PBI polymer on chambers and tooling are an especially good means to extend equipment wear.

PBI polymer is an amorphous thermoplastic that may be easily cleaned from surfaces and tooling when used in a temporary application. Polar solvents as *n,n*-dimethylacetamide (DMAC) and *n*-methylpyrrolidone (NMP) are known to work well for PBI polymer removal. Coatings rework is dependent upon the substrate and the curing condition. Removal is possible at room temperature; however, the addition of heat will accelerate removal.

It is well known that several thermal resistant polymers exist in commerce. These systems include both amorphous and thermosetting. Several have been demonstrated alone or as blends for temporary applications and are shown in the following Table 2, PBI is identified #4.

Table 2. Thermal resistant polymers and their properties.

#	Polymer	Cure Method	Thick (um)	Therm. Resist (°C)	Water Resist
1	Epoxy	UV	<20	>275	Yes
2	Rubber	Evap.	<15	>250	Yes
3	Poly-phenylene	Evap.	<10	>330	Yes
4	Imidazole	Evap.	<5	>450	Yes
5	Biphenyl Sulfonate + Polyester	Evap.	<10	>300	No
6	Acrylic	UV	<20	<250	Yes
7	Silicone	Catalytic	<10	>300	Yes
8	PAI	Evap.	<10	>300	Yes

### B. Vacuum Processing

One of the most challenging processes to overcome with a temporary polymeric adhesive is a simultaneous high vacuum with thermal condition. For most materials, reduced pressure conditions affect their physical chemistry properties by reducing the melting and boiling point. This applies to polymers, however, not all will express the same sensitivity. High vacuum conditions on materials at temperatures below their glass transition ( $T_g$ ) will have less affect than if the temperature is raised to above that level. Therefore, crystalline materials should outgas lower when the thermal condition is below their  $T_g$ , and if amorphous, below their softening point (SP). This information may be applied by selecting a material with a  $T_g$  or SP above the process conditions, as described below for a CVD (Fig. 5).

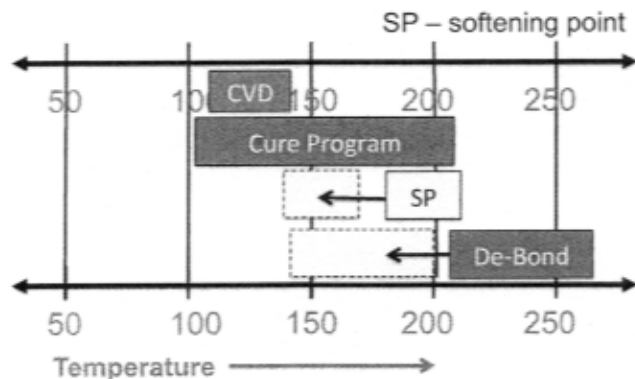


Fig. 5. Material selection based upon SP &gt; process (CVD).

The addition of barrier materials may also be used to suppress the migration of gaseous by-products in the adhesive. These substances exhibit low permeability as expressed as the measured gas passing through a specific polymer film of given thickness per day at 1 atm pressure ( $\text{cm}^3\text{-ml}/\text{day}\text{-atm}$ ). Barrier polymers are macromolecules, which exhibit the ability to significantly restrict the passage of gases, vapors, and liquids [13]. They are widely used in the packaging industry for food

preservation and other protection. Different polymers offer different permeabilities to different gases (Fig. 6).

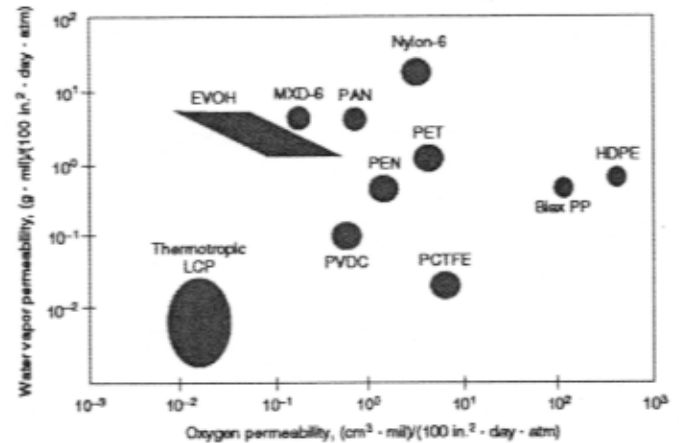


Fig. 6. Permeability data for a variety of polymers. Excerpt with permission [14].

Using barrier polymers in a system may offer benefits, provided the material is compatible and matched with the desired gas to suppress. Nylon-6 is a well known polyamide, similar to polyamide-imide (#8 in Table 2) with good water resistance, yet the material is very permeable to water vapor as shown in Fig. 6. It is common to have such trade-offs when selecting polymers to match the needs of a particular process.

### C. Low Stress

Stress is a measured property of thin substrates, which begin to bend and curl as a result of forces from the device build onto the substrate. As the substrate is thinned, stability from the substrate is removed and the internal forces from the device build become more exaggerated. When adhesives are used, their application and cure may also introduce stress. This is especially true for thermoset polymers where curing causes condensation of the system to a reduced form. Cross-linked molecules are more closely packed resulting in a reduced occupied area, shrinkage, and subsequent bowing of the substrate.

Stress testing is best conducted by applying the adhesive or coating to a thin substrate and curing. Once cured, the thinned substrate is put onto a flat surface and its deflection from that surface is measured, usually in mm. Example thin substrates include glass coverslips or other items that are <100um thick.

### D. Cleaning

One of the most important properties of the wafer adhesive is its ability to be easily removed (cleaned) from the surface, leaving the substrate in a pristine condition. Usual cleans practices involve the application of solvents or aqueous mixtures followed by an alcohol or water rinse. Typical cleaning practices for processing silicon 300 mm wafers uses a single-wafer cleaning tool with the flow described in Fig. 7.

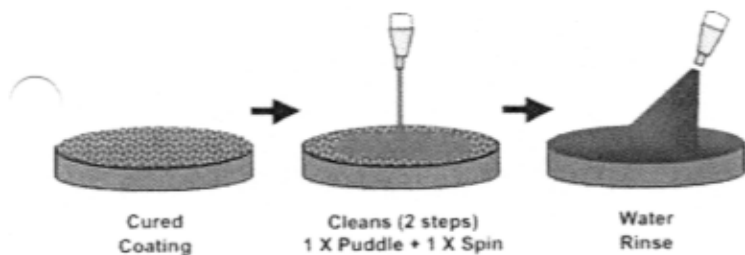


Fig. 7. Process flow for cleans following wafer de-bond.

When planning to use temporary adhesives for semiconductor processing as described in Figs. 1-2, it is generally assumed that a cleaning step will be included. As of the date of this publication, several committees comprising members of the semiconductor community are in review of this practice [15]. It is generally accepted that de-bonding and cleaning is preferred to be conducted while the product wafer is supported on a tape (film frame). This practice requires the cleaning chemistry and process to be fully compatible (safe) with the chemistry of the tape (Fig. 8 & Table 3).



Fig. 8. Process flow for cleans while product wafer is supported on tape (film frame).

Table 3. Cleaning compatibility on existing tape (film frame).

Adhesive Type	Cleaning	Tape Safety	Cleans Process
Rubber, Olefinic Polymer	Non-polar solvent	Yes, RT limited time	Short time, Cleaning - unknown?
Acrylic	Polar solvents	Limited (most)	Cleaning - unknown?
Polyimide	Polar solvents	Limited (most)	Cleaning - unknown?
Silicone	Specialty blends	Limited, attacked	Cleaning - unknown?

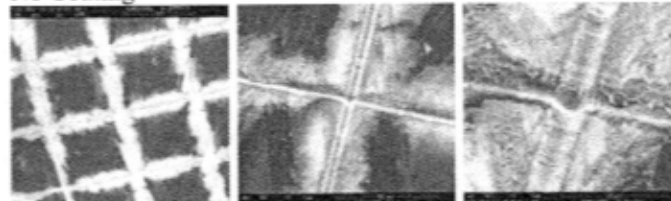
Although it may be known what cleaning agents should be used to remove temporary adhesive and residues from product wafers, it is believed that limited compatibility exists with the tape media. Due to the limited safety with the tape media, the cleaning process may need to be adjusted to reduce such effects (i.e. reduce temperature or time), or a special tool must be used to maintain separation of the cleaning chemistry from the tape media. This activity is under investigation.

#### Aqueous Soluble

Aqueous soluble coatings and adhesives offer an ease and

safety in their use. Water-washable coatings are used in laser dicing. Surface protection includes the use of an aqueous soluble coating, rinsed after laser processing, to remove debris from the heat activation zone (HAZ) [16]. Thin protective coatings are preferred to minimize interaction with the laser and its contact to the substrate in the HAZ. Thin coatings may help to reduce beam spreading in the HAZ, resulting in a desirable minimum kerf width.

#### No Coating



#### Coating Applied

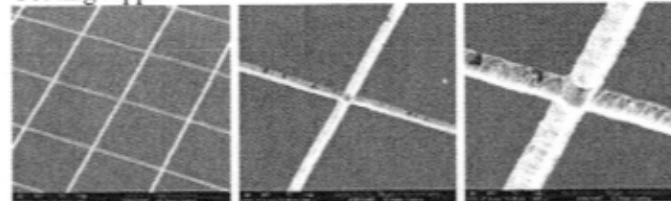


Fig. 9. Example SEM photos of aqueous soluble coating use to support laser dicing; no coating (above) &amp; coating (below).

The primary reasons in using aqueous cleaning practices include environmental safety and cost reduction. Whether it be cleaning with water or detergents, the chemistries are non-flammable, non-toxic, and do not generate evaporative material to trigger air permit requirements. Subtleties exist in aqueous cleans, and many believe it to be more challenging to control than organic solvents. Effective aqueous systems are built with additives that prevent irregularities during processing. Detergents can be mixed with tap water while rinsing with purified water. Ingredients in the detergent mix with contaminants in tap water to prevent metal precipitation, inhibit corrosion, and stop scale build-up. Because aqueous strippers become dirty during use, it makes sense to reduce water use and lower operating costs by reserving purified water for rinsing.

Detergents are being accepted for high performance stripping and selectivity, especially where large substrates are being processed. Certain companies are providing aqueous-washable temporary coatings and adhesives with simple cleaners in concentrated forms for semiconductor and other challenging markets [17]. Mixing at 3-10%, filtering, and then heating is simple and consistent with current practice. Using detergents for stripping PR and temporary adhesives is the fastest way to reduce costs by as much as 50%, and further, to reduce or eliminate the need for waste management.

#### F. Low Cost of Ownership

Although it is a target to transfer to HVM the many

temporary adhesives currently under investigation, it is likely that most will remain in an exploratory capacity due their high cost of ownership (COO). When conducting comparisons of one technology vs. another, a relative COO comparison is made with assumptions. Starting with SEMI E35 [18], a screening comparison is conducted as a ratio between COO<sub>2</sub> and COO<sub>1</sub> and canceling many of the variables due to the assumptions of similar yield, internal costs, scrap, life, and maintenance (Fig. 10).

Item	Definition
FS	Fixed Costs
RS	Recurring Costs
YS	Yield Cost (scrap)
L	Equipment Life
T	Throughput
Y	Composite Yield
U	Utilization

$$COO = \frac{FS+RS+YS}{L \times T \times Y \times U} = \frac{\text{Costs}}{\text{Product}}$$

$$\frac{COO_2}{COO_1} = \frac{\text{Technology 2}}{\text{Technology 1}}$$

Fig. 10. Variable identity from SEMI E35 & comparison.

## II. EXPERIMENTAL

### A. Equipment

Metrology data is generated by a *XP-1* stylus profiler, *AFP-200* atomic force profiler, and a *Xi-100* optical profiler [19]. Where applicable, equipment settings include a 5 mg stylus load, minimum 4 mm distance, and speed of 0.5 mm/sec. For cleaning tests, a Hg probe using a dot and ring contact, model 802B-150, an HP 4140B picoammeter source supported by an MDC measurement system with an I-V plotting program @ 10 mv steps from 0-1V [20]. Typical I-V plots are produced to compare trends and to study breakdown voltage of the protective film. Analytical equipment used in material characterization includes SEM (Hitachi 4700), Energy dispersive X-ray Spectroscopy (EDS), FTIR with ATR (Spectrum 100, DGTS detector, ZnSe coating accessory, Perkin-Elmer [www.perkinelmer.com](http://www.perkinelmer.com)). Modified thermogravimetric test methodology for outgas is conducted by typical laboratory scales (+/- 0.1mg). UV cure equipment includes the Intelli-Ray 400 microprocessor controlled light curing system (Uvitron International, [www.uvitron.com](http://www.uvitron.com)).

### B. Materials

For subsequent analytical testing, quartz substrates as are chosen and prepared at Daetec along with 100-200 mm (4-8") silicon wafers (1-0-0, ~525 μm) re-manufactured from Wollemi Technical, Inc. (Taiwan, [www.wollemi.com.tw](http://www.wollemi.com.tw)). Materials used include commercially available spin-coated adhesives and other developmental products produced at Daetec [21]. Coatings are produced on a Brewer Science, Inc. CB-100 spin-coater, while spray and encapsulation uses custom tooling designed at Daetec.

PBI polymer is prepared in DMAC (6-13%) and spin-coated onto silicon wafers cured according to Table 4 and measured for thickness. A second set of PBI polymer is prepared in n-n-

dimethylacrylamide (DMAA) ~10% solids with 5% Irgacure 2022 relative PBI polymer, coated onto silicon wafers, and cured by UV at 60sec, followed by thermal outgas 250C, 5min. DMAA is used with applications where UV cure followed by thermal is conducted for thick coatings. UV initiators include common free-radical based systems as Irgacure 2022 (BAPO/α-hydroxykeone).

Table 4. General cure schedule for PBI polymer coatings.

Step	Temp (°C)	Time (min)
1	90-110	<5
2	175-250	<5
3*	250-325	<5

\* used to achieve low-outgas conditions

A detergent washable temporary coating/adhesive is prepared at different concentrations varying from 22-40% solids and tested for thickness vs. spin-speed. After applying to silicon substrates, cured, they are tested for stress by coverslip bending. To separate samples of the aqueous washable coating/adhesive, varying amounts of barrier polymer is added and dissolved, coated onto silicon, cured, and then subjected to lab-TGA analysis for % outgas. The barrier polymer is selected from a long list of candidates and demonstrated experience in working with these substances, including their solubility to form a homogenous solution.

## III. RESULTS

PBI/DMAC solutions to produce coatings/adhesives on silicon follow thickness measurement as stated in Fig. 11. The PBI coated substrates are tested for their amount of outgas up to 300 °C and one sample is set aside for TGA testing. The results of these are shown in Figs. 12-13.

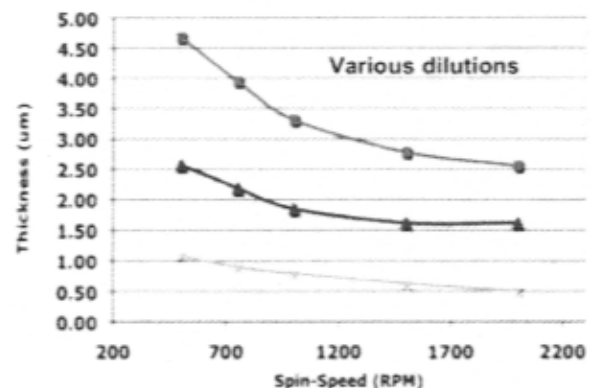


Fig. 11. Spin-speed curves for PBI coatings. The differing curves reflect various solution dilution.

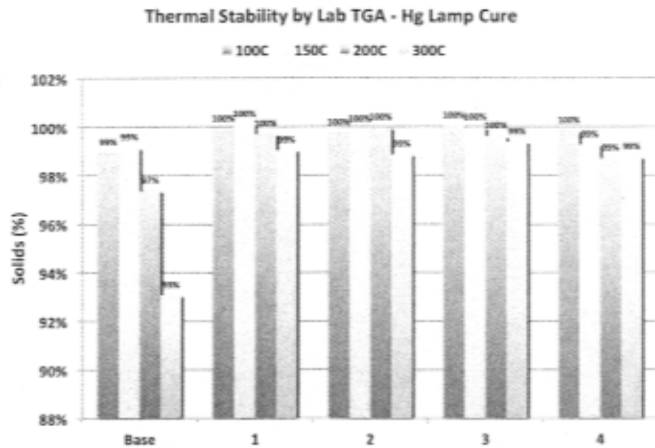


Fig. 12. Modified TGA results to 300 °C using different UV exposure levels. Stability range 99-100% for higher exposure.

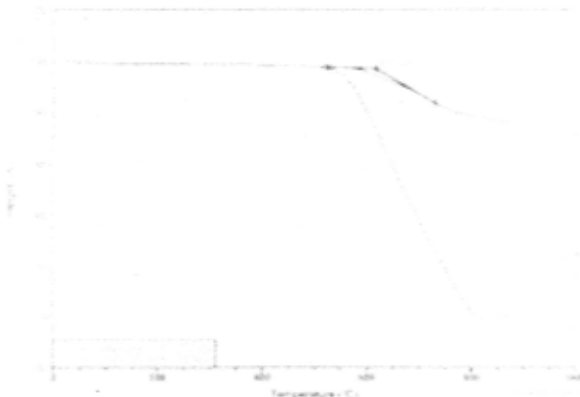


Fig. 13. TGA curve of PBI polymer, thermal resistance >500 °C in air and >600 °C in N<sub>2</sub>.

Results for the detergent washable coating/adhesive is given in Fig. 14, stress in Table 5.

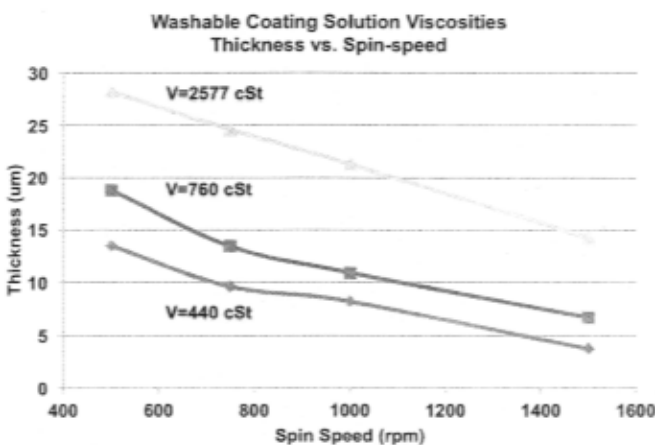


Figure 14. Spin-speed curves for aqueous washable coatings. The differing curves reflect various solution dilution.

Table 5. Results of stress measurement of various coatings. Use of the coverslip technique with >1mm cured adhesive.

Item	Cure	Stress (mm)
DMAA (pure)	UV	> 16 (breaks)
Urethane in DMAC	Evaporative	< 3
Aqueous Washable Blend	Evaporative	< 3
PBI/DMAC	Evaporative	< 3
PBI/DMAA	UV	3-5

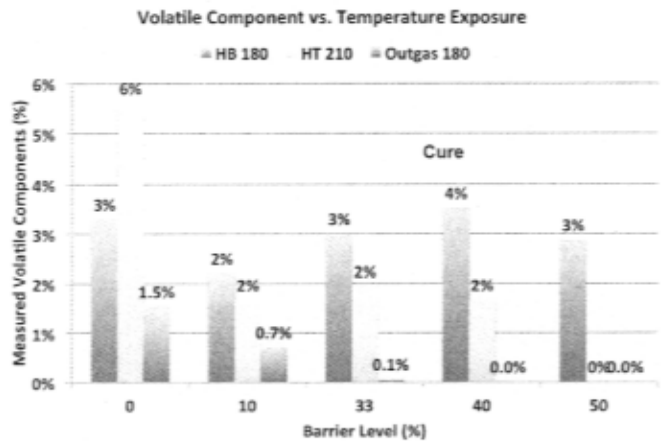


Fig. 15. Outgas measurement with barrier addition.

To demonstrate COO comparison, an adhesive technology change is reviewed at a solar manufacturing client. The solar company is currently scaling from a development capacity to a phase where equipment sets are specified and being ordered for their factories. The solar company manufactures a thin polysilicon substrate of <10um thickness. Due to thin wafer handling challenges, their current process involves the use of a liquid temporary adhesive Fig. 16.

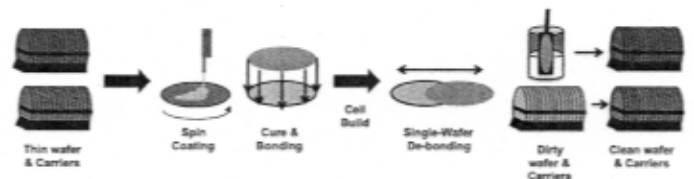


Figure 16. Manufacturing process using liquid temporary adhesive followed by thermal slide de-bond and cleans.

The liquid adhesive is toll-manufactured off-site, where cost is reflected as time and materials, a fraction of the cost as compared to commercially available spin-coat temporary adhesives. Further cost reduction is possible by considering a film adhesive applied by lamination methods (Fig. 17) and the subsequent comparison of materials and equipment as shown in the diagram in Fig. 18. Cost of materials and tooling with tooling represented as a factor of materials (Table 6). The

COO comparison conducted for film vs. liquid adhesive (Fig. 19) and representing tool costs as a factor of materials is shown in Table 7, with final calculation and % comparison in Fig. 20.

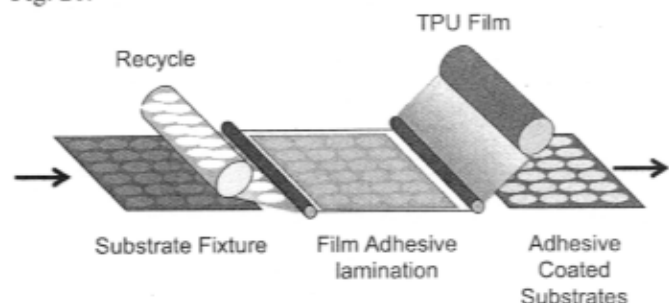


Figure 17. Film adhesive lamination process. Multiple substrates are laminated with a roll technique onto a substrate fixture containing carriers.

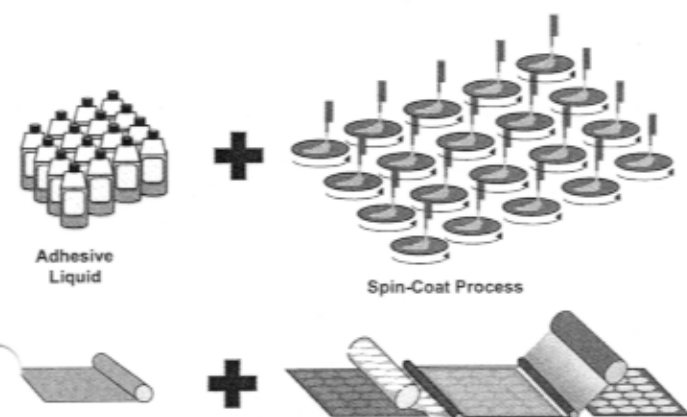


Figure 18. Comparison of technologies, liquid + spin-coating vs. film adhesive + lamination process.

Table 6. Costs of materials and tooling, with tooling represented as a factor of materials costs.

Adhesive Form	Materials Estimate (\$/wafer)	Throughput Estimate (wafers/day)	Tool Estimate (yr <sup>-1</sup> )
Liquid, spin-coat + cure	\$0.1850	(single) 288 (shared) 864	0.087 X RS <sub>1</sub>
Film, laminate	\$0.0125	28,800	0.38 X RS <sub>2</sub>

$$\frac{COO_2}{COO_1} = \left[ \frac{FS_2 + RS_2 + 0}{L \times 33T_2 \times Y \times U} \right] \times \left[ \frac{L \times T \times Y \times U}{FS_1 + RS_1 + 0} \right]$$

Figure 19. Comparative COO for film and liquid adhesive.

Table 7. Details of variables for COO<sub>2</sub> vs. COO<sub>1</sub>, liquid vs. film adhesive with stated assumptions.

#	Definition	COO <sub>2</sub> vs. COO <sub>1</sub>	Explanation
FS	Fixed Costs	FS <sub>2</sub> = 0.38 X RS <sub>2</sub> FS <sub>1</sub> = 0.087 X RS <sub>1</sub>	\$Roll = 38% film \$Coaters = 8.7% liquid
RS	Recurring Costs	RS <sub>2</sub> = 0.07RS <sub>1</sub>	\$Film = 0.07 X \$Liq
YS	Yield Cost (scrap)	YS <sub>2</sub> = YS <sub>1</sub> = 0	Polysilicon, low cost
L	Equipment Life	L <sub>2</sub> = L <sub>1</sub>	Same life
T	Throughput	T <sub>2</sub> = 33T <sub>1</sub>	1 Roll = 33 coaters
Y	Composite Yield	Y <sub>2</sub> = Y <sub>1</sub>	Same yield
U	Utilization	U <sub>2</sub> = U <sub>1</sub>	Same maintenance

$$\frac{COO_2}{COO_1} = \frac{(0.38RS_2 + RS_2)}{33(0.087RS_1 + RS_1)} = \frac{0.038RS_2}{RS_1} = 0.0027$$

Figure 20. Final comparative COO calculation for film and liquid adhesive. Scaling costs for film adhesive is ~0.3% of the cost of a liquid adhesive (reduced toll costing considered).

#### IV. DISCUSSION

Temporary adhesives exhibiting high thermal resistance, low outgassing and low stress have been demonstrated and discussed. Aqueous soluble candidates have been presented for debris control in high temperature laser dicing and with tape frame attachment of thin wafers after de-bond. When scaling from R&D to HVM, COO must be considered as early as possible. For simple review practices, a comparative COO analysis can be used for screening one technology over another.

Applying the COO comparison screen for two different temporary adhesive technologies in a HVM scaling effort for a solar manufacturer has proven our application. At the time of this publication, film adhesive manufacturers have been selected and testing is going forward in manufacturing. Early-stage equipment modification for the lamination process has occurred. The transition from liquid to film represents a single-wafer move to batch (multiple wafers coated simultaneously). The same attention is now occurring for the de-bond practice.

Extreme temporary adhesives that excel in performance and cost reduction do exist. Selecting these candidates depends upon a strong process knowledge ability to select matching candidates, and a willingness to explore new territory. When this process begins, the mindset moves from "what is

commercially available” to “what is possible”. Using a material cost reduction of 50% and tool reduction, significant COO benefits are possible.

## V. CONCLUSIONS

This paper presents data on the identification, formulating, and process demonstration for temporary adhesives that provide extreme performance and benefits. By understanding your process demands and overlaying this onto a technology roadmap, an adhesive may be identified to meet these objectives. Many other benefits begin to weigh-in after integration, including safety, waste minimization, and achieving green factory certifications.

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