

Thermal Resistant Thin Wafer Support Technology for 3DIC

Alman Law, Jared Pettit, Alex Brewer, and John Moore
Daetec, LLC, 1227 Flynn Rd., Suite 310, Camarillo, CA 93012 USA (805) 484-5546
(jmoore@daetec.com, www.daetec.com)

ABSTRACT

High temperature processing in microelectronic operations includes plasma deposition, dielectric curing, and annealing. Engineering polymers are chosen based upon sufficiently high Tg. Few materials can withstand temperatures beyond 400°C without suffering some level of degradation. With careful formulating, composite coatings can resist temperatures >500°C with limited outgas and have demonstrated coatings that support processes at 600°C. While processes that involve temporary wafer bonding operate much lower, many polymers can exhibit serious processing problems as outgassing and loss of the materials' properties. Many barriers exist to manufacturing integration, including high cost, poor yield, and poor throughput. As the demand continues for smart phones, 3DIC becomes a required process to manufacturing the devices needed to operate these units. One such technology, DaeBond 3D™, supports processing temperatures to 350°C while bonding near room temperature and de-bonding in a batch process while thinned device wafers remain affixed to film frames [1]. This paper will discuss several examples of thermal resistance for 3DIC processing.

Key words: thermal analysis, outgas, TGA, Tg

INTRODUCTION

Microelectronic manufacturing requires the use of thermal resistant polymers. Two of the most thermal resistant are polybenzimidazole (PBI) and polyimide (PI). Both exhibit a glass transition (Tg) above 350°C. The Tg is that temperature where a material changes from crystalline to amorphous. These materials are represented at the top of the temperature index of the performance triangle (Fig. 1).

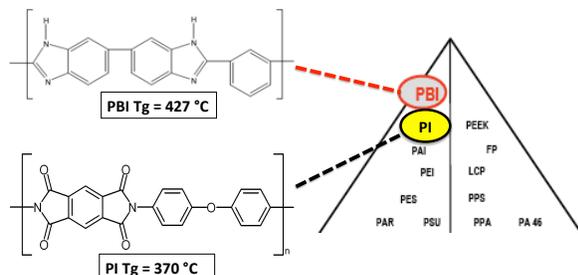


Fig. 1. Performance triangle showing polymers with a temperature index of >150°C, amorphous (left) and crystalline (right).

Although thermal resistance may be a key consideration for a polymer's use in electronics, many other properties help define a material an application, such as transparency and chemical compatibility. The ability to build a system with combinations of these characteristics will define a polymer product for use as temporary adhesives in chip stacking, flexible substrates as displays, and dielectrics.

Thermal Resistance

Polymers used in electronics have a thermal budget. Materials are chosen and prepared to rid the system of irregularities prior to processing. Thermogravimetric analysis (TGA) is performed to identify a material's irregularities subjected to a thermal program in air or inert conditions while measuring its change in weight. Thermo degradation is shown at the inflection (change in slope). TGA values of PBI and a vinyl-silicone coatings are presented as 617°C and 405°C, respectively (Fig. 2), with the coating appearance.

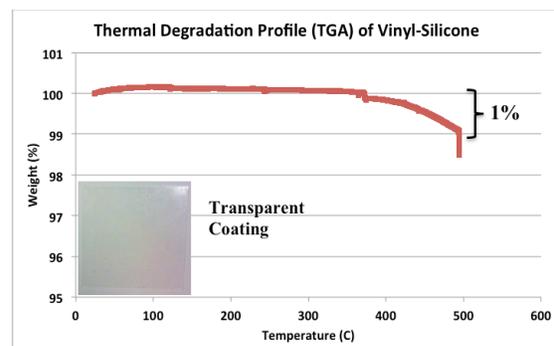
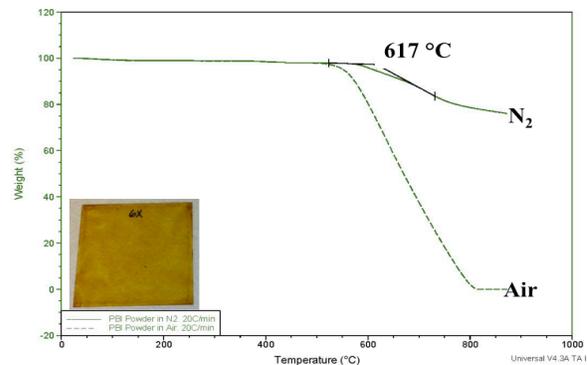


Fig. 2. TGA curves of coatings of PBI (top) and vinyl silicone (bottom) showing thermal resistance >600°C in N2 and up to 500°C, respectively.

While TGA is popular, other modes of thermal analysis exist, including thermomechanical analysis (TMA), and differential scanning calorimetry (DSC) [2]. TMA measures expansion and contraction under conditions of temperature, load, and environment. DSC measures heat evolved or absorbed during heating, cooling or isothermal conditions. These tools are used to acquire valuable data to predict a material's behavior during a process. Color change can predict thermal resistance while the product may still retain the majority of its physical and chemical properties. In most cases, it is discouraged to accept changes in appearance as it is the first indication of thermal oxidation, crosslinking, and a potential to leave residue and stains during its removal.

Transparency

Color development may be triggered by multiple sources to include the polymer chemistry, environment, or impurities from the casting solvent. For example, one PI chemistry of unique design is claimed to exhibit ~50% transmittance at 420nm and increasing in its clarity with increasing wavelength [3]. A transmission spectra is given for a clear PI, identified as Novastrat 400, SRS ManTech (Fig. 3). Improving transparency depends upon the product chemistry. Thin and flexible substrates that exhibit high thermal resistance and >90% transparency at <400nm is in demand for high yield optical devices, solar panels, and displays.

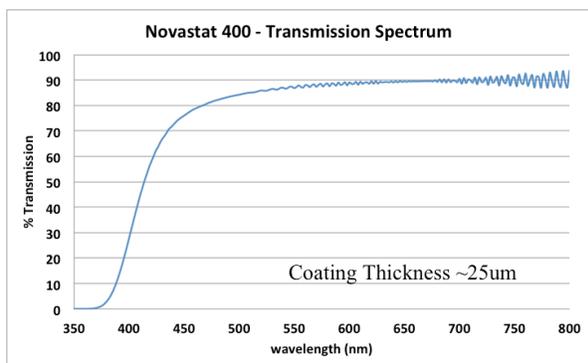


Fig. 3. Transmission spectra for a clear PI where %T = 27% at 400nm for a thickness of ~25 μm as coated and cured on glass (courtesy SRS Mantech).

Dissolving PI commonly uses aprotic solvents such as n,n-dimethylacetamide (DMAC) and n-methylpyrrolidone (NMP). Solutions are prepared near 20% solids with heating and mixing. Since many crosslinking PI systems start with polyamic acid, residual acid and monomer will remain. As curing continues, these trace impurities contribute to color.

Polymers in 3DIC

A wide range of polymer types have been reportedly used in wafer bonding for three-dimensional integrated circuits (3DIC). These polymeric substances include rosin-urethane [4], silicone [5], rubber [6-7], and

acrylic [8]. Wafers are bonded to carriers to prevent substrate bow and cracking during thinning and backside processing. The temporary adhesive is commonly applied to the wafer, bonded, processed, and then de-bonded and cleaned (Fig. 4)

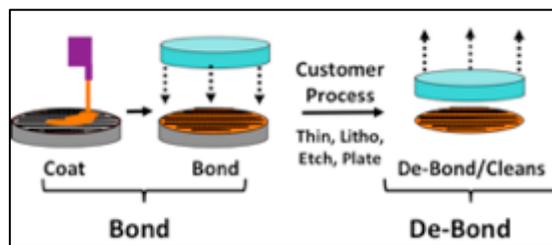


Fig. 4. Process of bond and de-bond is shown.

Thermal resistant polymers for 3DIC are temporary and as such, must not become permanent during exposure to chemicals and thermal programs. The use of a carrier during bonding enables good surface planarity, low total thickness variation (low TTV), and reduces both internal stress and wafer bow during grinding.[9-12] Thinning uniformity TTV at ≤0.5% is maintained throughout processing.[13-14] De-bonding practices vary from chemical solvation, thermal slide, or laser ablation, lasting anywhere from min to hours.

Temporary Bonding

Polymers used in electronics for 3DIC applications commonly surround temporary applications. DaeTec has several options with thermal resistance to 350°C.

Table 1. List of temporary bonding products.

DaeCoat™	Description	Thermal
200	Transparent film; peel de-bond	>300°C
210	Polyimide film; peel de-bond	>350°C
310	Tunable adhesive for polyimide; peel de-bond	>350°C
350	Coating w/tunable adhesion	>300°C
515	Water washable	>300°C
550	UV cured, water washable	>250°C
615	Thermoplastic, detergent washable (DaeClean™ 150)	>200°C
620	Thermoplastic, detergent washable (DaeClean™ 150)	>250°C

These products enable multiple approaches to temporary bonding thin and fragile substrates. Temporary bonding products are used for flexible organic light emitting diode (OLED), thin glass, foils, wafers, and components (die). Table 2 describes the work unit types, application, DaeCoat™ products, and the suggested configuration to be used.

Table 2. Applications of DaeCoat™ products.

Work Unit	Market	DaeCoat™	Method
Organic Film	OLED, flexible displays	350	Cure on carrier, bond w/pressure
Organic Film (cast)		310	Cure on carrier, cast & cure liquid
Thin glass	TFT LCD	350	Cure on carrier, bond w/pressure
Foil	OLED, flexible displays	350	Cure on carrier, bond w/pressure
Wafer	3DIC	350, 615, 620	Planarize wafer w/550, cure on carrier, bond w/pressure
Die (chip)		350	Cure on carrier, bond w/pressure

With the possible exception of wafers, all work units mentioned in Table 2 are de-bonded by peeling practices. In most cases, DaeCoat™ 350 is used with proper adhesion adjustment to allow simple and non-damaging practices to occur. Adhesive remains on the carrier, recycled/cleaned, and returned to the line for bonding to another work unit. By measuring and tuning adhesion using a roll-style tool (Fig. 5), displays are peeled from a laser trimmed glass carrier (Fig. 6).

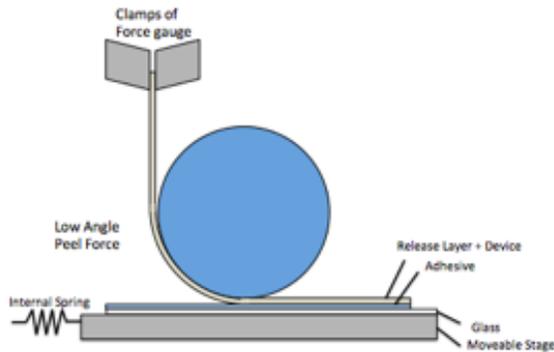


Fig. 5. Peeling model using roll-style tool.

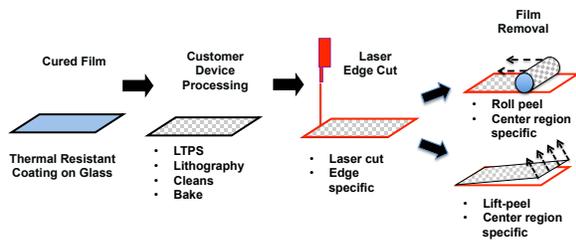


Fig. 6. Process flow for temporary bonding of thin films in display manufacturing.

DaeBond 3D™

Using similar materials as described in Tables 1&2, DaeBond 3D™ is a novel batch-processing thin wafer handling system. Device wafers are planarized with DaeCoat™ 515, bonded to a carrier with DaeCoat™ 350 (tunable adhesion force), and processed through the customer's line. De-bonding occurs by capillary driven penetration into the bond line to effect separation while the device wafer is supported onto a taped film frame. A tape-safe chemistry, DaeClean™ 300, is used in a simple wet bench tool offering low cost and throughput defined by the size of the cassette and tank (Fig. 7).

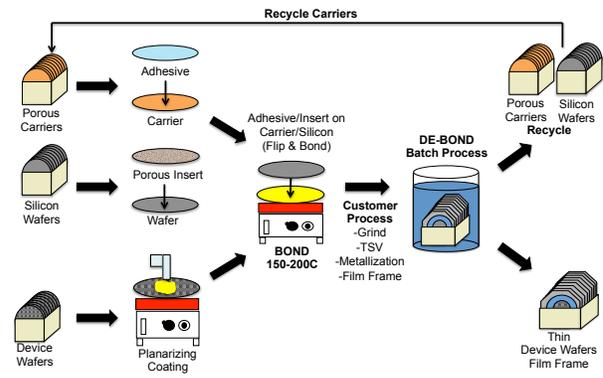


Fig. 7. DaeBond 3D™ technology flow.

Carrier de-bonding occurs in Tank 1 by liquid penetration to break the edge seal and migrates swiftly through the porous coating until saturation causes a drop in adhesion. Cassettes of film frames holding device wafers proceed to tank 2 for final washing (Figs. 8 & 9).

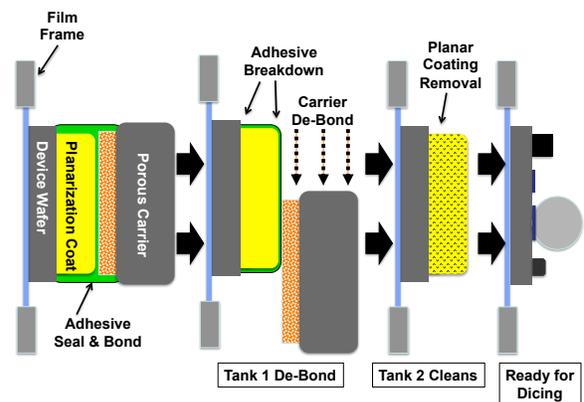


Fig. 8. Step-wise carrier de-bond & wafer cleans.

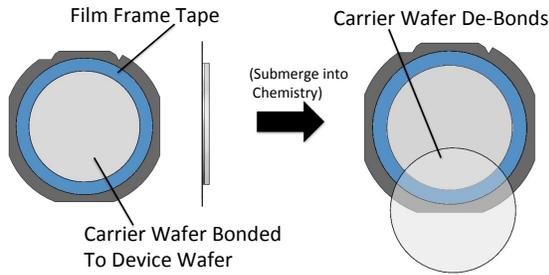


Fig. 9. Carrier de-bond from the taped film frame.

EXPERIMENTAL

Materials

For process testing, remanufactured silicon substrates at diameters of 100-200 mm (4-8") of known crystal orientation and thickness (1-0-0, ~525 μm ; Wollemi Technical, Inc. Taiwan, www.wollemi.com.tw). Materials used include: a) DaeCoat™ 515 (planarizing coating), b) DaeCoat™ 350 (adhesive w/tunable force), and c) DaeClean™ 300 (cleaner) [15]. Process chemistries include: TMAH (0.26N), isopropanol (IPA), n-methylpyrrolidone (NMP), various dilute mineral acids, and sulfuric acid copper plating bath. Tape products for film frame applications include: Lintec and Nitto-Denko.

Equipment

Coatings are produced on a Brewer Science, Inc. CB-100 spin-coater, while spray and encapsulation uses custom tooling designed at Daetec. Metrology data is generated by a XP-1 stylus profiler, AFP-200 atomic force profiler, and a Xi-100 optical profiler. Where applicable, equipment settings include a 5 mg stylus load, minimum 4 mm distance, and speed of 0.5 mm/sec. Bonding and de-bonding equipment is designed at Daetec for radiation and thermal cure. Thermal analysis equipment includes Discovery TGA and Discovery DSC from TA Instruments.

RESULTS

TGA on a rosin-based adhesive in Figs. 10-11 suggesting a preferred 110 C cure for ~15min to outgas before processing. DSC also shows reaction kinetics by cure temperature to achieve cure completion (Fig. 12).

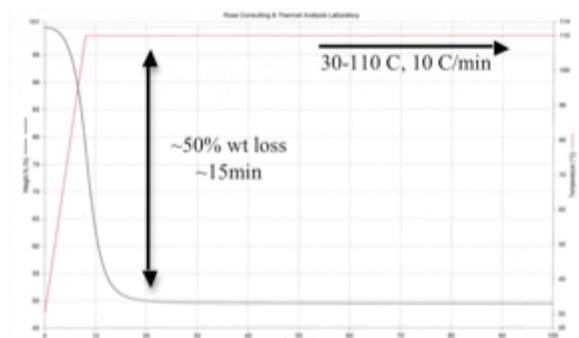


Fig. 10. TGA outgas during post-baking.

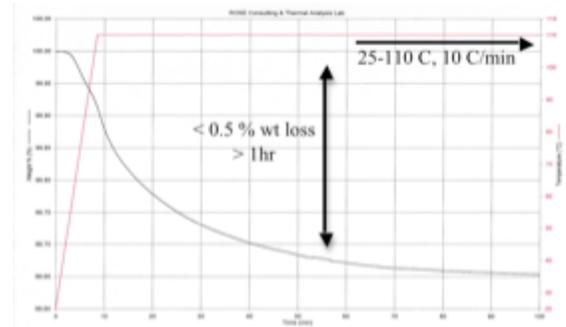


Fig. 11. Outgas TGA following post-bake.

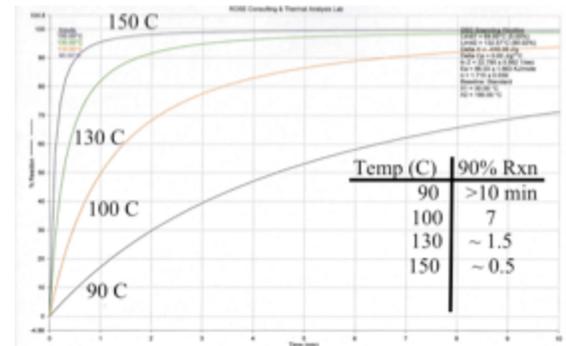


Fig. 12. DSC reaction completion vs temperature

Polyimide is shown to degrade transparency with thermal exposure to 450°C. In separate experiments, PI was peeled from glass substrates and tested for tensile strength. In one experiment, a commercial product was exposed to temperatures up to 450°C, held for 10hrs, and then tested for tensile strength. A drop in tensile strength is observed and compared to the manufacturer's information (Fig. 14).

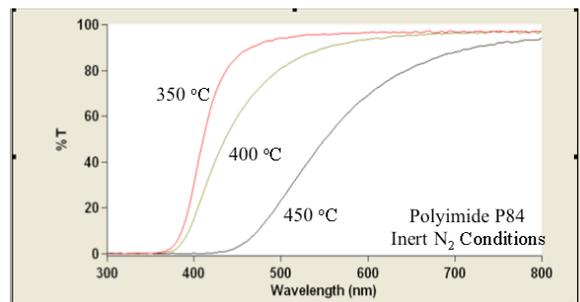


Fig. 13. UV/VIS of PI, drop in %T with temperature.

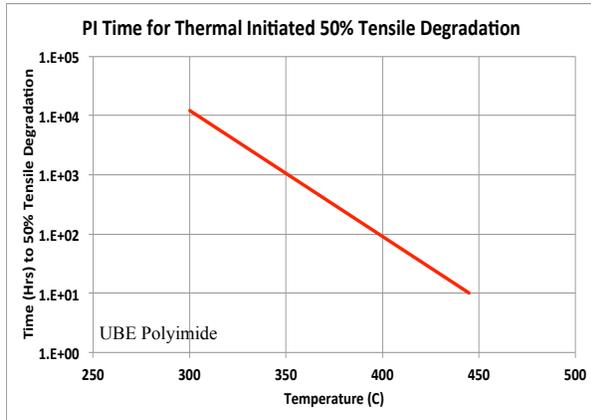
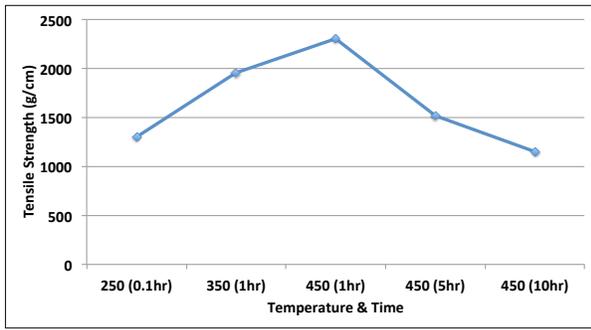


Fig. 14. Tensile strength of polyimide with heat exposure. U-varnish tensile strength of ~10um films exposed to 450°C for up to 10hrs (top) is compared with manufacturer information (bottom).

Experiments with silicone resins attempted to boost thermal resistance using various catalysts and nanoparticles. Catalysts were chosen from common sulfonic acid, benzylic amine, and nano sized ceramic and metal. Thermal exposures were conducted between 250-450°C measuring condensation (crosslinking) as thermal outgas by weight change (Fig. 15) with improvements using nano materials (Fig. 16).

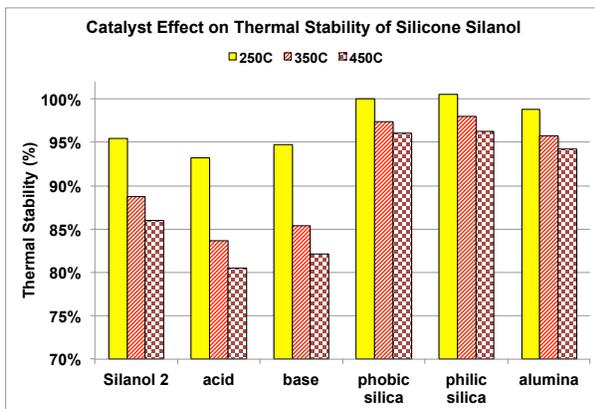


Fig. 15. Catalytic silanol condensation between 250-450°C measuring thermal stability as % weight change.

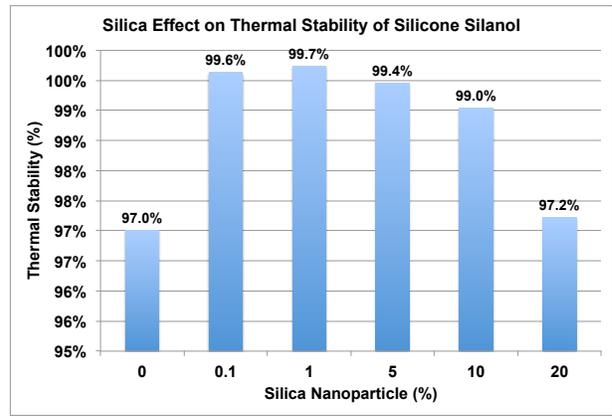


Fig. 16. Catalytic condensation of silanol chemistry by nanoparticles to 450 °C showing good stability with as little as 0.1 % addition to achieve >99% stability.

Silanol mixtures were coated on glass using similar cure programs as described earlier for polyimide. Once completed, the films were subjected to a number of thermal programs (Fig. 17) to demonstrate thermal stability and followed with UV/VIS (Fig. 18).

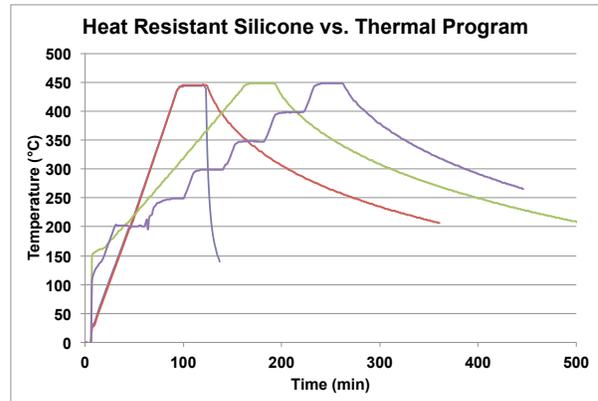


Fig. 17. Temperature program of silanol experiments.

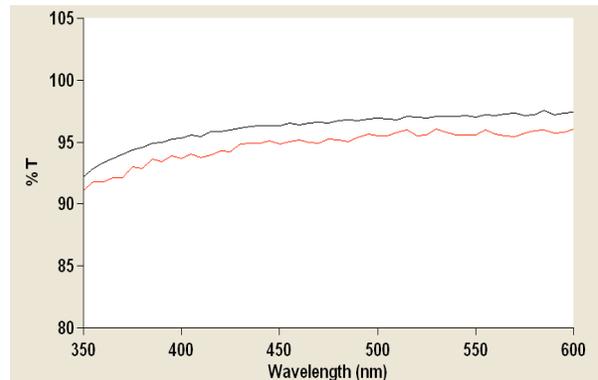


Fig. 18. UV/VIS of silanol films.

The ability to boost thermal resistance of an acrylic and using a rapid UV cure process is demonstrated by the addition of PBI using as low as 10% w/w as polymer is indicated in Fig. 19.

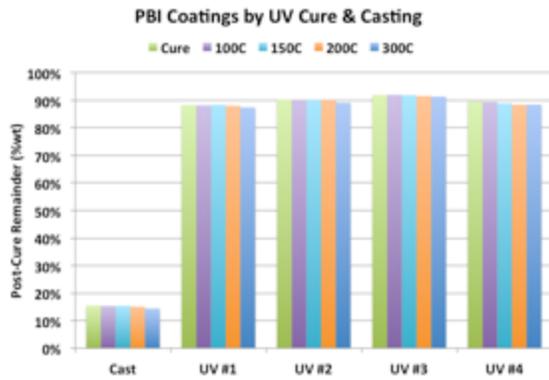


Fig. 19. UV curing of an acrylic with PBI as compared to casting, exhibiting thermal resistance to 300C.

Vinyl silicones are commonly used in elastomeric applications. These systems use vinyl resins, cross linkers, and catalysts. Many other additives may also be used for desired properties in the final product. As more additives are used, there is a likely increase in outgassing, depending upon the temperature of the process. By exposing the cured product to a post bake condition, residual materials can be reduced or eliminated depending upon the final temperature that is chosen of processing (Fig. 20).

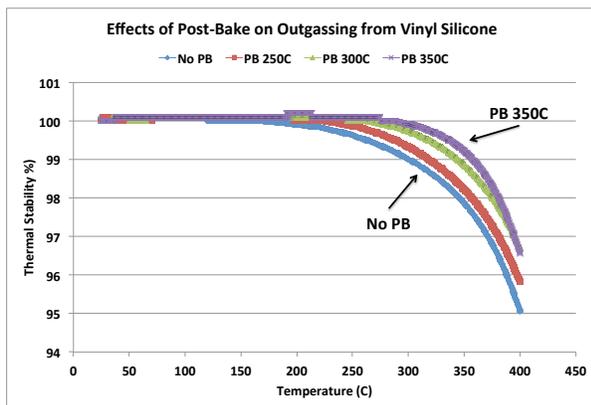


Fig. 20. Increasing thermal stability by the use of different post bake temperatures, all at 30min.

DISCUSSION

This paper presents several observations of thermal analysis of different polymers. Increased thermal resistance can occur with proper attention to the polymer type and the process. The main driver for thermal outgas and degradation reduction is to ensure the product will satisfactorily withstand conditions in a vacuum oven, plasma machine, or related process.

One of the most challenging processes to overcome to minimize outgassing is with high vacuum and heat. 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 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 in a CVD (Fig. 21).

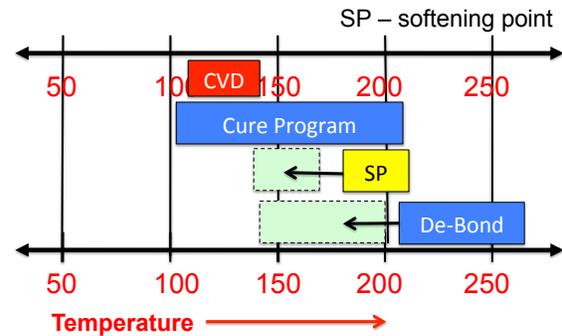


Fig. 21. Material selection using SP > process (CVD).

The addition of barrier materials may also be used to suppress the migration of gaseous by-products in the adhesive. Barrier polymers are macromolecules, which exhibit the ability to significantly restrict the passage of gases, vapors, and liquids. 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 (cm³-ml/day-atm). Experiments indicate barrier values of 10% offer benefit in support of CVD processes (Fig. 22)

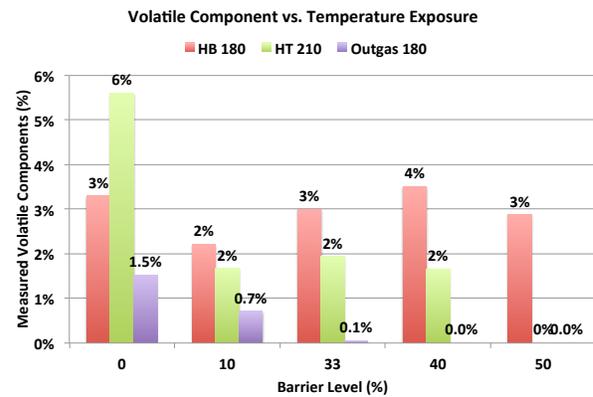


Figure 22. Outgas vs. barrier % in a CVD operation.

CONCLUSIONS

This paper presents data and process suggestions to reduce the occurrence of outgassing from polymers used in electronic processes. With proper choices of polymer and conditions, adverse thermal conditions can be abated. We have observed thermal stability of acrylics, silanols, and silicones pushed to 450°C. This stability supports plasma etch and related processes used in 3DIC processing, such as the description

provided here for the DaeBond 3D™ technology.

ACKNOWLEDGEMENT

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