Washable Coatings for Packaging Processes

Alex Brewer[a], Alex Laymon[b], and John Moore[a]
[a]Daetec, LLC, 4069 Calle Tesoro, Camarillo, CA 93012 (jmoore@daetec.com, www.daetec.com)
[b]DPSS Lasers Inc., 2525 Walsh Ave., Santa Clara, CA 95051 (alaymon@dpss-lasers.com)

Abstract
Many packaging processes require the protection of components while another application is conducted. This may include a planarizing coat over large topography while a deposition, bonding, or curing step is completed. Washable coatings are materials that protect the substrate during thermal or mechanical activities and are simply washed away using readily available and green products, such as water or detergent. Washable products are not new, an example includes laser washable coatings that remove debris from the heat activation zone (HAZ) during scribe and break processes. In such cases, thermal resistance is desired as high as possible. The chemistry of washable products includes polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) [1]. While these are excellent choices for consumer packaging (e.g. laundry packets, vitamins), they are best used in electronics for room temperature processing due to their cross-linking upon exposure to heat and metals. Alternatively, thermal resistant and washable products (e.g. DaeCoat™ 515) are available that provide protection to ≥300°C without the aid of mechanical tooling [2]. Planarizing coatings over metals can be thick (>300µm) as in cases where solder bump encapsulation is needed during dielectric coating and cure or when another die is thermal compression bonded. This approach has been demonstrated with washable temporary bonding adhesives in protecting C4 bumps while bonding micro-bumped die onto FPGA interposers [3]. Washable adhesives have been created for thermal and vacuum driven processing as EMI/RFI shielding in a PVD tool. Such coatings are applied to porous substrates, affixing die, processing, and removal by water washing [4]. Success in these and related temporary applications depend upon matching the chemistry of the washable coating with the process. Our experience in creating these solutions will be discussed as well as the criteria for using temporary washable coatings.

Key words
Coatings, detergent, green products, solubility, thermal resistant, water,

I. Introduction
Coatings are film-forming substances, which protect a substrate against potentially damaging elements as well as enhancing its appearance. The global coatings market is expected to reach nearly $200b in revenue by 2022 growing at a CAGR of 5.4%, representing over 30b liters of product annually [5]. Nearly 50% of all coatings are applied in Asia, also a major electronics market. This paper addresses the niche application of temporary coatings in electronics packaging. Temporary coatings are applied, processed, and washed away without harm to the substrate. Most washings mentioned in this paper are based upon water. These temporary coatings perform planarizing, bonding, priming, sawing, and laser dicing.

A. Washable Coatings
A washable coating is applied to sustain a process and removed later (e.g. temporary adhesive, Fig. 1).

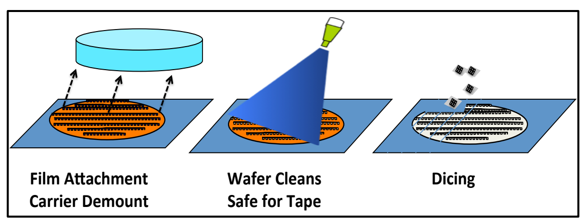


Fig. 1. Washable coatings include temporary adhesives that are removed before singulation.

B. Chemistry
Washable coating chemistries may include ingredients as simple surfactants and salts. Should special properties be needed, these get narrowed down to a few materials worthy of classification as a coating. Non-thermal resistant examples include PVA and PVP. These polymers exhibit film-forming character. PVA further exhibits molecular arrangement and close packing which act as barrier materials to prevent outgas or as sealant materials. Where flexibility is needed, trace solvent or high molecular weight additives may be used as plasticizers and to improve its properties and appearance (Fig. 2).

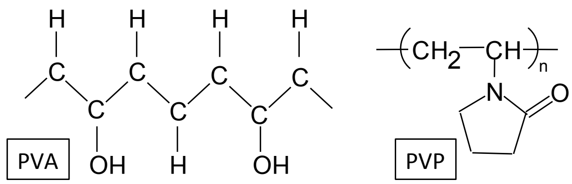


Fig. 2. Idealized molecular representations of PVA and PVP, both contain repeating functional chains.

Water-soluble forms of PVA and PVP are readily available in liquids, solids, and films. Long chains of these molecules exist as random intermingled mixtures. It's common for PVA is to have acetate groups at periodic points in the carbon chain. These groups extend from the chain and create branching, which leads to cross-linking. Cross-linking creates larger molecules with increased molecular weights, higher crystalinity, density, and increased thermal and chemical resistance (Fig. 3).

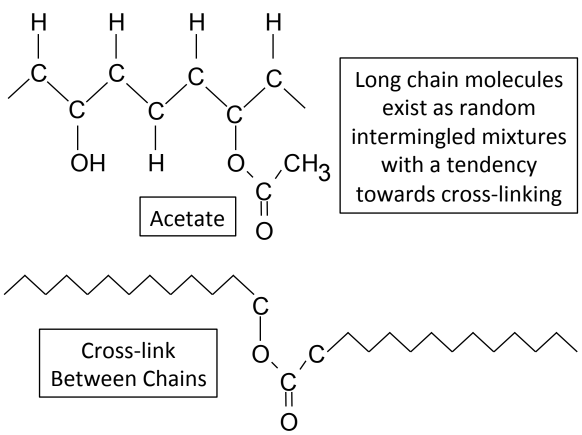


Fig. 3. Branched functional groups create cross-linking that affects the product's final properties.

B. *Cross-linking*

In practice, both PVA and PVP molecular species contain functional groups that can lead to cross-linking. Crosslinking creates a network within the mixture that fixes the material into place, a condition desired for permanent systems in electronics. This is ideal for thermosetting polymers as acrylics, polyimides, and epoxies. With some exceptions, cross-linking is discouraged when the polymer must be washed away. This sort of unwanted reactivity will increase system rheology, premature expiration, and residue during washing. Preventative practices include cold storage and avoiding exposure to heat, metals, and oxygen.

Thermosetting washable systems do exist [2]. These are desirable as they cross-link to provide thermal resistance, low outgas, and are easily washable. Thermal and UV initiated systems are presented (Table 1).

Table 1. List of available washable cross-linking coatings.

DaeCoat™	Chemistry	Cure	Thermal Resistance	Washing	Application
357	Silicone	UV	>300 °C	DaeClean™ 300	Planarize, bonding, protection
365	Silicone	Thermal	>300 °C	DaeClean™ 300	Bonding, protection
555	Acrylic	UV	>300 °C	DIW	Bonding protection
575	Acrylic	UV	>250 °C	DIW	Bonding protection

C. *Property Preservation*

Matching chemistry with a desired process defines a robust condition. For thermal resistance, preference is given to polymers contain phenyl functionality. For example, styrenated species provide thermal resistance and maintain water-solubility (Figs. 4 & 5).

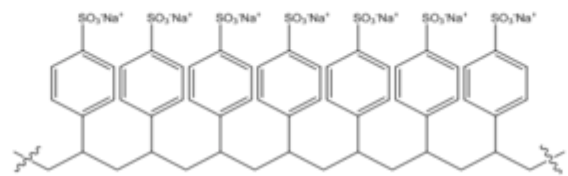


Fig. 4. Syrenated polymeric species exhibit good thermal resistance and water solubility.

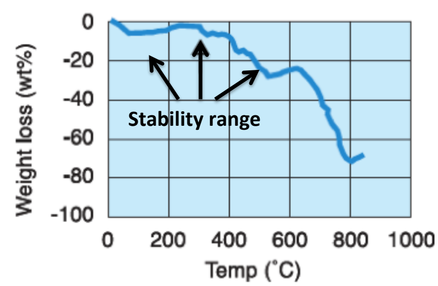


Fig. 5. Thermal analysis of styrenated polymers; water solubility is preserved at >500°C exposure.

Many washable coatings are prepared in aqueous media whereby their condition must be preserved for long durations in storage without the occurrence of bio fouling. Biological growth can occur in wide ranging pH conditions as known by mold growth in acidic conditions and bacterial in neutral or alkali. Adding solvents or biocides do work but increase the complexity of the mixture and often interfere with coating properties or attack the substrate. Most of Daetec's aqueous products do not contain additives as their polymers exhibit natural biocide properties.

D. *Applications*

Many uses exist for washable coatings, one example includes temporary bonding. Two active stages exist using a carrier and adhesive: bonding and de-bonding (Fig. 6).

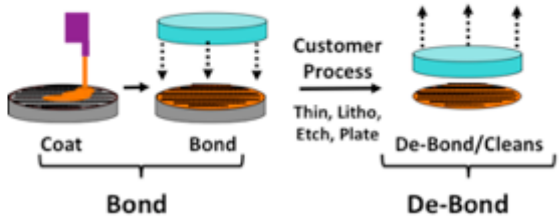


Fig. 6. Two active stages to the use of any temporary adhesive and carrier, bonding and de-bonding.

In upstream semiconductor processing, wafers are ground and polished to at least 100um while front side devices are protected during backside processing. Many adhesive chemistries are used for thin wafer handling, including: a) rubber/olefin [6-7], b) acrylic [8], c) silicone [9], d) polyimide [10], e) rosin-urethane [11], and BCB [12]. During de-bond, the device substrate must be washed free of all adhesive, sometimes requiring great effort.

A thermoplastic detergent washable adhesive, DaeCoat™ 615, exhibits thermal resistance >200°C. The product is commonly used for wafer thinning with carriers with device substrates as GaAs and Si, proven at <25um thickness, and uses metal friendly aqueous detergent for cleans, DaeClean™ 150, classifying it as green [2] (Fig. 7).

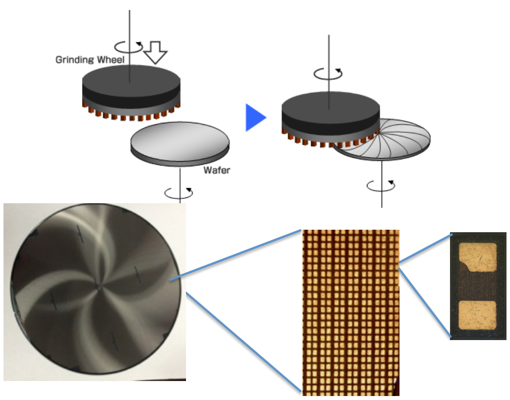


Fig. 7. Temporary bonding process involving thinning by grind/polish (above) and parts singulation.

A common property in coatings for electronics applications is thermal resistance. A simple water washable product for laser processing is DaeCoat™ 525. This product has >300 ºC resistance. The product is applied, cured, and laser processed. During rinsing, the heat activation zone (HAZ) is rinsed with water to produce clean surfaces [13] (Fig. 8).

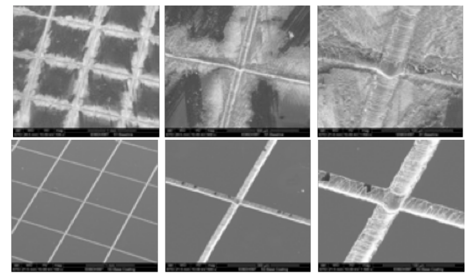


Fig. 8. SEM photos of laser processing baseline (top) and with DaeCoat™ 515 coating (bottom).

Washable silicone coatings as DaeCoat™ 365 are used to temporarily affix small die, process, and de-bonded/washed with a safe cleaner as DaeClean™ 300. This has been proven to reduce inherent bow/warp on FPGA interposer substrates and resisting a solder reflow for bonding micro-bumped chips [3]. The coating encapsulates existing C4 bumped features, is flipped and bonded to a porous carrier (Fig. 9), bond to micro-bumps, and then is debonded from the carrier and cleaned (Fig. 10).

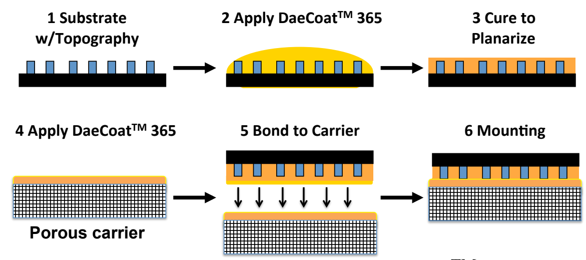


Fig. 9. Washable silicone coating, DaeCoat™ 365, is used for small die affixing and bump encapsulation.

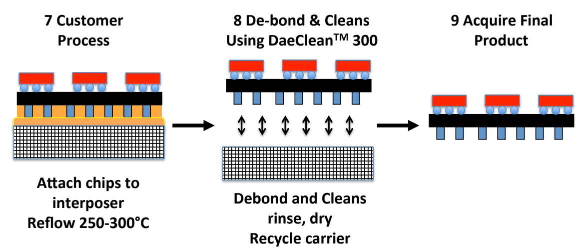


Fig. 10. Die processing, demount, and cleans using DaeClean™ 300.

II. Experimental

A. Materials

For subsequent analytical testing, quartz substrates as are chosen and prepared at Daetec along with 100 mm (4-8”) silicon wafers (1-0-0, ~525 µm) re-manufactured from Wollemi Technical, Inc. (Taiwan, www.wollemi.com.tw). Materials used include commercially available spin-coated adhesives and other developmental products produced at Daetec. UV-cure applications are conducted with free-radical resins available from BASF.

B. Equipment

Coatings are produced on a Brewer Science, Inc. CB-100 spin-coater, while thick coatings with slit tooling and spray washing 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. Modified thermogravimetric test methodology for outgas supported by laboratory electronic gauges (+/- 0.1mg). UV cure equipment is Intelli-Ray 400 microprocessor system (Uvitron International, www.uvitron.com). Adhesion measured by force gauge with software (www.mark-10.com) using method (Daetec SOP #45, ASTM D3330).

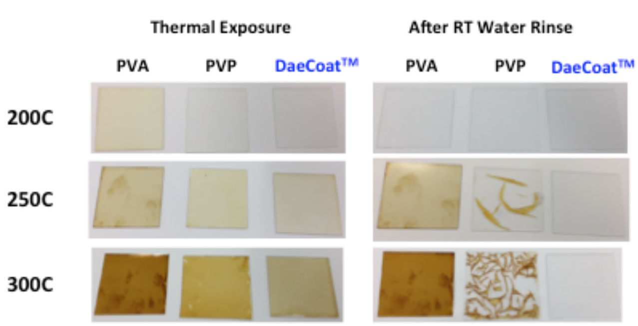
Laser processing uses a 355nm UV system, 3 Watt at 30 KHz at 25nsec pulse width (100uJ per pulse) with at 20um beam width at working surface, entitled the *Samarai* laser system [14]. Grid patterns of 30 X 30mm size having each grid as 3 X 3mm. Scan speed is 300mm/sec with multiple passes (≤25) conducted to observe effects of processing.

III. RESULTS

A. Thermal Resistance

Coatings of DaeCoat™ 525, a water washable system for temporary protection and laser processing, is heated and subsequently rinsed with water. Coatings of PVA and PVP are included for reference. The observations are presented in Table 2.

Table 2. Thermal resistance test results on DaeCoat™ 525 compared with PVA and PVP. Summary table below.



Chemistry	Appearance Soft Bake (100°C)	Appearance Hard Bake (350°C)	DIW Washing RT, <15sec
DaeCoat™ 525	Clear	Brown	Clean
PVA	Clear	Brown	No Clean
PVP	Clear	Brown	No Clean

Thermal stability of DaeCoat™ 525 is >350ºC for oxygen/air environments and higher for more inert conditions (i.e. N_2, Ar, etc.). Coatings of 525 after various temperatures rinse easily with water while PVA and PVP cross-link at <250ºC and remain after washing. Summary table of these values are presented (Table 2).

DaeCoat™ 525 washable coating is applied to silicon, laser processed, and water washed. Multiple laser exposures of 25X were chosen as worst case. Results are compared to PVA and PVP (Fig. 11).

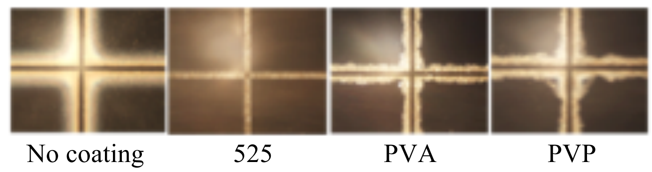


Fig. 11. OM images following washing after laser processing, DaeCoat™ 515 compare to PVA & PVP.

TGA of DaeCoat™ 615 suggests minimum thermal resistance at >200ºC (Fig. 12).

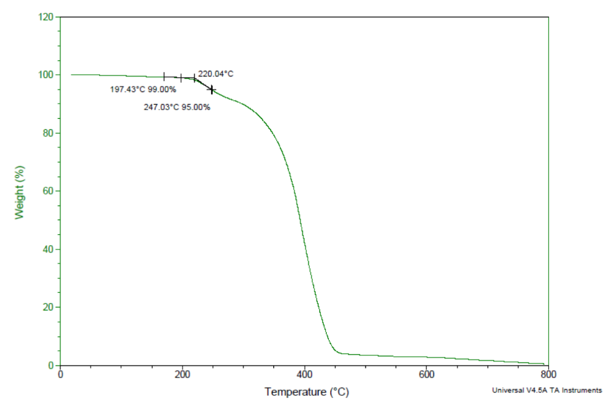


Fig. 12. Thermal stability is >200°C of DaeCoat™ 615 coating, a detergent washable adhesive.

B. Additives

Common tracer additives are tested as a fluorescent tag for the presence of the coating and can show defects in microscopy with the aid of UV (Fig. 13).

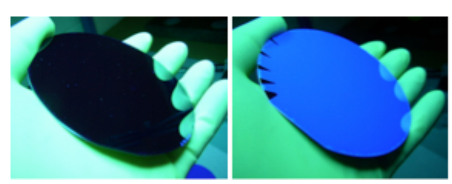


Fig. 13. Additives used as tracer dye in DaeCoat™ 615 detergent; left - no dye, right – with dye.

C. Processing

Grinding and polishing are demonstrated for wafers and quartz prisms using detergent washable adhesive, DaeCoat™ 615. Contour plots suggest a high coating uniformity TTV of <2um across wafer (Fig. 14), and proven cleans with DaeClean™ 150 in DIW (5%) during prism/glass polishing (Fig. 15).

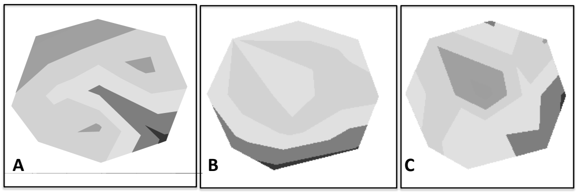


Fig. 14. Contour plots of A) bare wafer, B) bonded (before grind), and C) post-grind, DaeCoat™ 615.

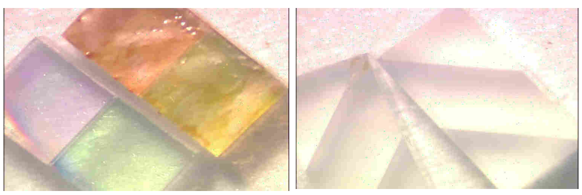


Fig. 15. Before (left) and after (right) cleans process for polishing using DaeCoat™ 615.

IV. Conclusions

Washable coatings are used throughout manufacturing to conduct detailed processing and achieve complete removal on demand. The choice of material must consider how the substrate is to be processed in order to reduce crosslinking and ensure no residue persists. DaeCoat™ products have been demonstrated for temporary adhesives, planarizing coatings, and washable laser solutions.

V. Discussion

Washable coatings that use DIW are being further explored in many different manufacturing processes. There is a strong emphasis for companies to present themselves as green and move away from the risks of chemicals. Several new areas are being explored using DIW water to process the coatings.

One exciting area of business is reduction in device geometry by limiting flow/bleed of capillary underfill (CUF). The fillet is limited by establishing a berm/barrier of a DIW washable product, DaeCoat™ 575. This product is applied by dispensing or printing technology using UV curing followed by a thermal step. The CUF is applied, cured, and then the 575 is washed. The CUF remains is a tighter space, reducing overall packaging size (Fig. 16).

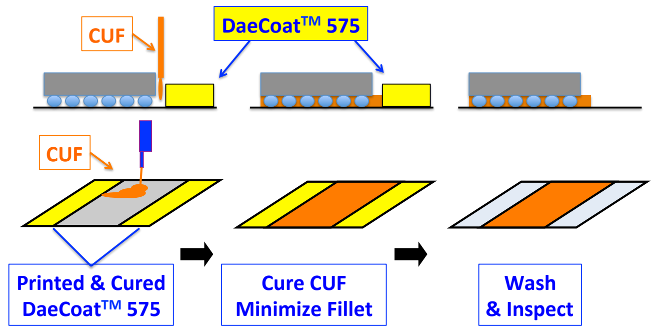


Fig. 16. Dispense/printed DaeCoat™ 575 establishes tight CUF geometries.

Hot DIW washable coatings reduce bow/warp in thin low temperature co-fired ceramic (LTCC) substrates by affixing the substrate to a porous carrier during high temperature encapsulant cure and solder reflow (Fig. 17).

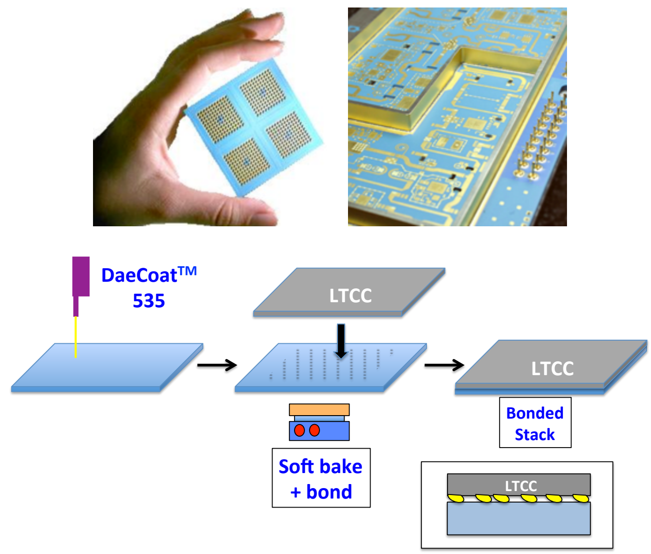


Fig. 17. LTCC substrates (top) are ≤100um thick and fragile. They are bonded to Daetec porous substrates using DaeCoat™ 535 hot DIW washable adhesive (below).

These two examples describe two DIW washable coating processes in electronics packaging. Others being designed and demonstrated include EMI shielding, molding compounds, and washable coatings for contamination control.

Acknowledgment

The authors thank the staff at Daetec and DPSS for their support in making this work possible.

References

[1] PVA and PVP are sold by Kuraray and Ashland Chemical, respectively (www.kuraray.co.jp.com, www.ashland.com).

[2] Washable coatings are available as DaeCoat™, a trade name of Daetec (www.daetec.com).

[3] P. Flynn & J. Moore, Optical Profilometry of Substrate Bow Reduction Using Temporary Adhesives, *Sematech 3DIC Metrology Workshop, Semicon-West Conf.* (2012).

[4] J. Moore, et al., High Volume EMI-Shielding Process for LGA and BGA Components, *IEEE Proceedings for EPTC,* Singapore (2015).

[5] Global Paints and Market Outlook (2014-2022), *Stratistics MRC,* www.strategymrc.com (June 2015).

[6] A. Smith, J. Moore, and B. Hosse, A Chemical and Thermal Resistant Wafer Bonding Adhesive for Simplifying Wafer Backside Processing, *Proceedings for GaAs MANTECH,* April 2006, pp.269-271.

[7] U.S. Patent No. 7,678,861, J. Moore and M. Fowler, March 16, 2010.

[8] U.S. Patent Applications 2009/0017248 A1 (2009), *Larson et al.*; 2009/0017323 A1 (2009), *Webb et al.*; and International Application WO 2008/008931 A1 (2008), *Webb et al.*

[9] U.S. Patent Nos. 6,869,894 and 7,098,152, March 22, 2005 and Aug. 29, 2006, J. Moore.

[10] PI is marketed as HD-3000 series non-photodefinable adhesives for wafer bonding, E. I. du Pont de Nemours and Company (www.dupont.com).

[11] U.S. Patent Nos. 6,869,894 and 7,098,152, March 22, 2005 and Aug. 29, 2006, J. Moore.

[12] BCB as Cyclotene™ electronic resins for wafer bonding, the DOW Company (www.dow.com).

[13] K.C. Su, H.H. Lu, S.H. Chen, C.D. Tsai, Y.C. Chou, b W.J. Wu, G.Q. Wu, and J.C. Moore, A Novel Water-Washable Coating for Avoiding Contamination During Dry Laser Dicing Operations, *Proceedings for GaAs ManTech Conference,* pp. 317-320, May 2007.

[14] Samarai UV laser marking system is a product of DPSS Lasers, Inc. (www.dpss-lasers.com).

