WHITE PAPER

Silver Epoxy Turns Black after an Oxygen Plasma Clean prior to Wire Bonding …but so what?

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ABSTRACT

In the early 1970s component manufacturers switched to epoxies for die attach in lieu of a eutectic attach. Resin bleed out was a common problem with these early epoxies and still is today. Resin bleed is difficult to see unless a filtered light source is connected to the microscope. The easiest and most effective manner to clean epoxy resin bleed, and other outgassed organic species, is to expose the assembly to a UV Ozone or an O_2 plasma treatment just prior to wire bonding. However, oxygen plasma turns the silver die attach epoxy black. Customers often take offense to this color change and hence O_2 plasma cleaning prior to wirebond in large microwave hybrids and for other product types is normally not performed. Argon plasma is used instead.

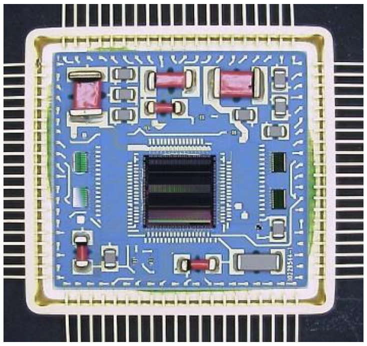
This presentation reviews the chemistry involved in the formation of “black epoxy” and how the silvery epoxy appearance can easily be restored, thereby allowing for a more aggressive clean prior to wirebond. Rework of wire no sticks or multiple wirebond attempts on the same pad is a major concern in the manufacture of large area Hybrids and RF MMIC microwave hybrids and a big contributor to expensive rework cycles. How to effectively clean up resin bleed and deal with the “black epoxy” is the subject of this white paper

Key Words: Oxygen plasma clean,UV Ozone, Resin bleed, black silver epoxy, Visual Inspection, MIL-STD-883 TM 2017 , Blue Light inspection methods

Rework is a major problem faced by all in this industry:

The manufacture and assembly of hermetic high reliability Hybrids, RF microwave modules, 5G technology and Class III medical implants is a very challenging undertaking involving many process steps, a myriad of materials and mile long BOMs. Epoxy dispense, component placement, wirebond and hermetic seal are the critical processes that all need to be optimized as each flow into the other and in the end determine product reliability and company profitability. Rework is every company's Achilles' heel. This "hidden factor" as they used to call it, is a substantial part of most cost overruns, schedule delays and diminished quality.

RF Microwave Module



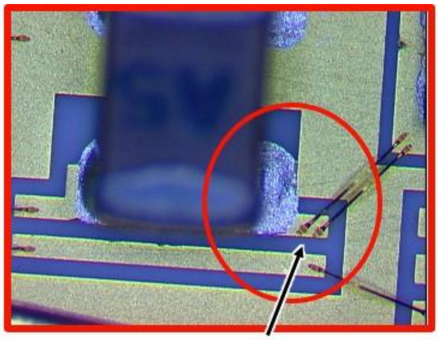
Thick Film Hybrid

Removal and replacement of ICs and MMICs (Monolithic Microwave Integrated Circuits) is especially problematic. This rework step involves locally heating of the component above the epoxy Glass Transition Temperature (Tg) of the epoxy underneath, getting a flat screwdriver or tool under the die and digging it out. This inevitably creates collateral damage in terms of loose FM/F.O.D (Foreign Material/Foreign Object Debris) as the die can shatter and cause unintended collateral damage to nearby components. These loose conductive particles are a major reliability concern in any cavity sealed device and is addressed in detail in all the MIL-STD-883 visual inspection test methods. The dried silver epoxy then has to be scraped clean and new wet epoxy dispensed. A new component has to be carefully placed and sent to the cure oven for a second time. Next comes wire bonding on a heated stage, maybe with the help of an off-line manual wirebonder. The hybrid then has to get caught up to the lot and sent through a second cycle of screen testing. Keeping track of all this for a military job is a nightmare and it's very difficult to put an accounting cost on a rework cycle. Individual rework of wires that don't stick or ones that are over bonded and break due to heel cracks is a little easier, but still problematic.

Wirebonding inside a hybrid or microwave 5G module is hard. Microwave assemblies in particular often contain 30 or more components with various bond pad metallurgies and differing heights within the hermetic module. Bonding to a clean, properly plated (50 micro-inches minimum soft Au) hard thin film ceramic is easy. Soft Teflon boards or ENEPIG on FR-4 are quite another matter. For those types of substrates the ultrasonic energy delivered to the wire during the bond cycle is attenuated into the soft board material and thereby greatly reduces the process bond window. For example, try sticking a deep access 0.7^{ths} Au wedge bond wire onto a soft PTFE substrate that has been soldered into place. These are the applications where surface cleanliness can be the difference between a high yielding auto wirebond process and numerous expensive rework cycles fixing wires and replacing components.

Lack of cleanliness is a major cause of rework

It is well understood that surface cleanliness prior to wirebond, or lack thereof, is a big problem faced by many followed closely by tracking and removal of FM and FOD, which is the result of excessive component and wire rework. A telltale sign of poor cleaning in a hybrid is the deformation or "squash" on a wirebond…ball, wedge stitch, doesn't matter. Overbonded wires are often the result of a wirebond operator cranking the ultrasonic power to do the job and scrub through the surface contaminant in order to get the wire to stick. This overbond leads to heel cracking or is rejected by QA for out of spec visual compliance to MIL-STD-883L TM 2017 (Pre Cap Inspection). Sometimes the wire doesn't stick and that's not good either. Beat up the bond pads on an IC bad enough and it will need to be replaced!

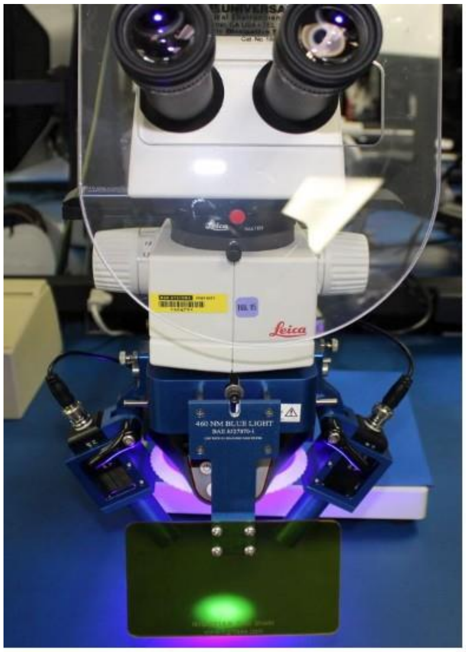


TM 2017 Violation wirebonds within 5 mils of epoxy fillet.

TM 2017 Pre Cap Visual Inspection is the required Mil Spec inspection document and the *de facto* industry workmanship standard for most high reliability commercial and medical products. In the latest release of MIL-STD-883L, TM 2017 para. 3.1.5.8.m states:

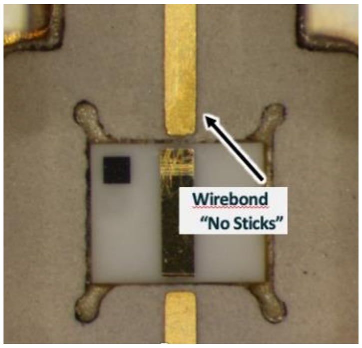
"Polymeric adhesive which may be material or residue as evidenced by discoloration within 5.0 mils of the outer periphery of a wire bond" is considered a rejectable condition.

The spec is specifically referring to resin bleed out and the reason for the 5 mils is that it's difficult to see visually, even at 60X using a conventional stereo zoom microscope. Resin bleed is only an issue when it gets on or near a wirebondable surface or wicks up onto the surface of an IC or MMIC.

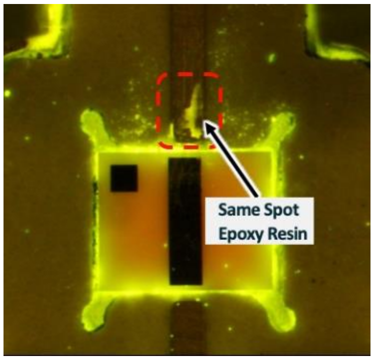


The “Blue Light” Special (patent #10,466,176)

Shown above is a filtered blue light fluorescence unit integrated with a bench top stereoscope, LEICA model M80. While fluorescence is commonly used to inspect conformal coatings, such visual techniques have previously proven ineffective for the detection of epoxy resins in microelectronics hardware. It is possible to readily visualize cured epoxy resins and many other contaminants on gold bond pads and other microelectronics components by visual inspection with a 460nm blue LED illumination and a 515 nm long pass filter.

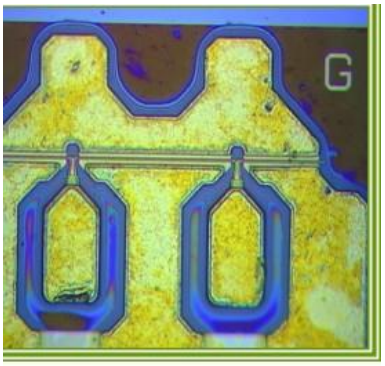


View under ambient light

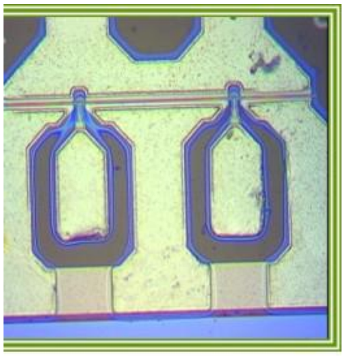


View under blue light

This inexpensive fluorescence microscopy method can be integrated into existing bench top stereoscopes and does not require the use of expensive and often destructive analytical techniques such as IR spectroscopy or XPS (REF 2).



Organic Resin on FET



After O2 Plasma Cleaning

Above is clear evidence of how a O_2 plasma treatment in a downstream plasma cleaner can effectively remove epoxy resin, which in this case had wicked up onto the surface of a FET (Field Effect Transistor). The two gate pads require a 0.8^{ths} gold wedge bond and the only chance to stick that wire with reasonable squash is to have a surface that is pristine in terms of cleanliness. Other surface organics on all the wirebondable surfaces within the hybrid or RF module are cleaned up as well and that makes wirebonding so much easier. The result is less rework.

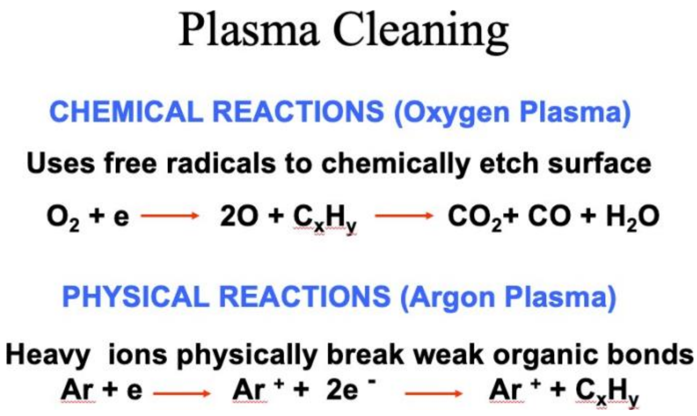
Plasma Cleaning

Microscopic surface contamination in general, sometimes just 20-50 A° thick, and organic in nature, is the result of previous process steps such as; outgassed volatiles from the oven cure, residual contamination on the substrate or die that was not cleaned by the supplier, residual plating chemicals left over from the board supplier and/or microscopic residue from previous wet chemical processing steps, especially for soldered components. It's very common and the reason why everyone plasma cleans prior to wirebond. Oxygen plasma also does a great job cleaning up resin bleed out.

When epoxies were first introduced in the early 1970's, as an alternative to a eutectic bond, UV Ozone cleaners were very popular at the time to clean up the inevitable bleed. In order to create ozone a chamber with low pressure mercury lamps emitting radiation at 1849 and 2537 A° wavelengths is needed. At these frequencies O_2 molecules in the air break up to form atomic oxygen and ozone O_3 along with a host of free radicals ($3O_2 + UV \Rightarrow 2O_3$), which then react with hydrocarbons on the surface.

Ozone is considered dangerous and gas must be exhausted from the area. This may be the reason UV ozone cleaners fell out of favor over the years and have been replaced by plasma cleaning chambers.

Oxygen plasma is extremely effective for the removal of organic surface contamination, however most process engineers shy away from this because the O_2 plasma turns the silver epoxy black. Most companies opt for argon plasma instead and never consider O_2 plasma as an option if using Ag epoxy. Argon can be effective and is a good alternative, but it may not be as effective. In an oxygen plasma the O_2 molecule chemically combines with the organic and the resultant CO and CO_2 gases are exhausted during the pump down cycle. It’s especially good for cleaning resin bleed out. The mechanism for cleaning in an argon plasma is more akin to power washing your deck, where inert argon ions are used to physically knock atoms off the surface. These surface molecules fly around and are redistributed on the inside of the oven, and elsewhere or get sucked out during pump down.



Plasma Cleaning

CHEMICAL REACTIONS (Oxygen Plasma)

Uses free radicals to chemically etch surface

$$O_2 + e \longrightarrow 2O + C_xH_y \longrightarrow CO_2 + CO + H_2O$$

PHYSICAL REACTIONS (Argon Plasma)

Heavy ions physically break weak organic bonds

$$Ar + e \longrightarrow Ar^+ + 2e^- \longrightarrow Ar^+ + C_xH_y$$

<u>What causes Resin Bleed?</u>

The hybrid industry has long endured the problem of "epoxy bleed" from die attach adhesives. This phenomenon appears to be a separation of the epoxy constituents from the filler. The bleed out can be observed after wet epoxy is dispensed, or after the epoxy cure step, or maybe not until the part sits for a time on a heated work stage prior to wirebond. Capillary action from the porous ceramic substrates may tend to draw out the un-reacted species in some cases. It’s a problem that tends to come and go and is often lot related. Some colleagues have reported that a plasma clean followed by a vacuum bake prior to die attach helps to eliminate/control resin bleed.

The problem remains and often goes undetected because resin bleed is not always visible.

The bleed manifests itself as shiny or glassy appearing material flowing away from the edge of an adhesive fillet.. The chemistry that is involved in the attempts to repair or eliminate this problem is discussed below.

<u>"Chemistry Happens”</u>

The following discussion is presented with a silver filled, die attach epoxy as the primary focus - specifically the chemistry and experiences with Ablestik 84-1 LMISR4. But the general concepts discussed are applicable to practically all filled adhesives. A good general reference textbook on epoxies was published in 2005 by Licari and Swanson (REF1).

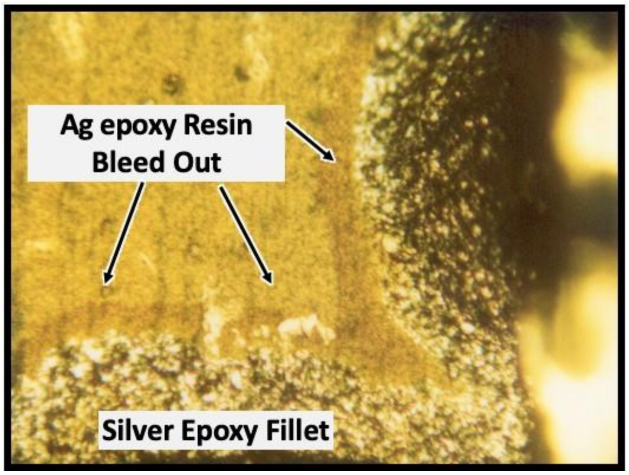
The formulation of the 84-1 system published by Henkel in the related Material Safety Data Sheet (MSDS Rev. 004.4) is as follows:

Silver flake	70 - 80%
Bisphenol-F Epichlorohydrin Resin	10 - 20
1,4 - Bis(2,3-epoxypropoxy)butane	05 -10
Dapsone: 4,4'- diaminodiphenylsulfone	1-5

Note the significant range that is permitted for each component - this variance can significantly factor into the performance of each lot of adhesive that is procured.

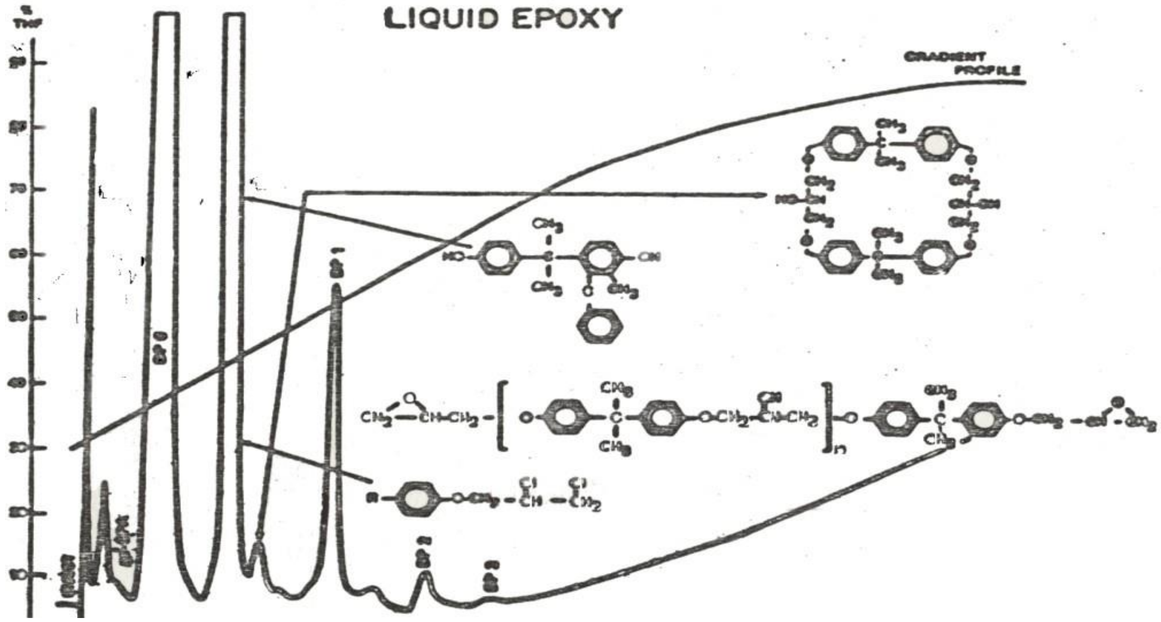
Resin Bleed:

Epoxy adhesives are a blend of: (1) an epoxy resin (usually a Bisphenol A or F), (2) a curing or cross-linking agent (usually a secondary or tertiary amine), (3) a filler - in this case silver flake, and (4) possibly some other additives to initiate cure, provide plasticity, lower viscosity, etc. as well as possible impurities. After cure the resin, cross-linking agent and filler are bound in place, i.e. the silver flakes of the filler cannot migrate. There are, however, times when not all of the "resin" is cured into the matrix. Cure times shorter than specified and inadequate temperatures due to oven overloading, or poor temperature control in an oven, can lead to incomplete curing. Un-reacted species from poor stoichiometry, other additives, such as a mono-functional epoxy (which has been added to alter viscosity or plasticity) and even pre-polymer precursors may not be chemically bound. One of the primary reasons for this is "steric hindrance", i.e. not all of the reactive sites in the polymer are physically available for reaction as other portions of a molecule could be blocking them. When this occurs, the un-reacted species is allowed to move freely within the body of the material. And when this non-reactant reaches the edge of a fillet, capillary draw will cause this resinous material to flow onto the substrate and more curing (or hardening) can occur. The net result is a clear film of "resin" that appears as a ring or edging around a fillet.



An examination of the molecular structures that make up the cured epoxy reveals an additional contributing factor for bleed. It should be noted that the 1,4-Bis(2,3-epoxypropoxy) butane component is essentially a linear molecule. The long, linear (and not branched) chain length that it introduces into a cured epoxy resin creates a greater diffusion path for un-reacted molecular species, i.e. the greater the cross link frequency or density, the smaller or more restricted the leakage paths. This particular "additive" to the Bisphenol F formula is probably done to impart viscosity control, flexibility and impact strength, qualities that are definitely a must for the finished microelectronic device.

Precursor residues in epoxy resins have been detected via Gel Permeation Chromatography (GPC) and reported over forty years ago by others such as Waters Assoc. in a published product data sheet.



Batch to batch variations

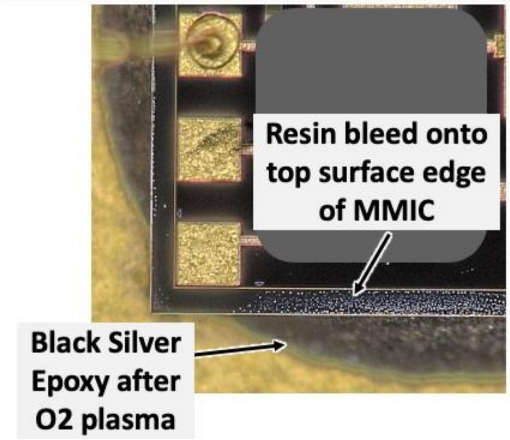
As shown in the GPC there are more than the four identified molecular structures - only one of which is the desired species. Note that the GPC is that of Bisphenol A - it differs from the "F" structure by the methyl groups on the methylene bridge. Nevertheless, these two structures have essentially the same polymerization processes and are susceptible to the same unwanted side products, residues and contaminates that can complicate the die bonding operations.
Attempts to require "cleaner or more purified" resins for epoxy formulations for MIL-STD-883 Test Method 5011 were fought by the supply industry, as it was their position that they needed the liberty to "adjust" batch to batch variations by using epoxies of different oligomers and/or additives (not to mention the batch to batch variations in the unwanted molecular species). Hence, bleed can vary from time to time in an established die attach process when a new lot of adhesive is introduced to the line.

As noted above, this discussion is focused on the Ablestik 84-1LMISR4 formulation which was developed to aid machine dispensing via the addition of a thixotropic agent such as fumed silica. Once cure has occurred, the presence of the thixotrope is partially defeated by the high cure temperature. Thixotropic agents rely on high surface area and intermolecular forces, such as hydrogen bonding and Van der Waal forces. But above 100^{o}C, these forces are overcome. Intermolecular bonds break down and individual molecular species can migrate.

What causes the epoxy to turn black after exposure to O_2 Plasma?

Unfortunately, when silver epoxy is subjected to an oxygen plasma it has the effect of ablating the epoxy resin coating the filler in the fillet. The oxygen plasma can then form a black silver oxide on the surface of the silver flake as it becomes exposed during the plasma treatment. Silver (Ag) exposed to oxygen at temperatures below 195_{o}C forms the covalent compound Ag_2O which is black in appearance.

$$4Ag\,(s) + O_2\,(g) \rightarrow 2Ag_2O\,(s)$$



There is an additional, minor contributing factor that may add to this blackening of silver filled adhesives that warrants mention. In years past, the silver flake was reported to be treated with a lubricant during the milling or rolling process that forms the thin flakes. The lubricant, probably stearic acid or other high molecular weight organic material, is also oxidized in the oxygen plasma process and there is an outside chance that a carbonaceous residue remains. This would most likely be a function of the duration of the oxygen plasma exposure. It has also been reported that some of the silver flake appears to be exposed and pieces of it can be dislodged upon physical probing. This could be a possible concern from the perspective of loose FM or FOD and should be carefully reviewed.

The Get Well Plan…Argon plasma and more heat

The blackening or oxidation of the fillets is generally considered an unacceptable "side effect" of the cleaning process. Even though there is nothing in the Pre Cap TM 2017 inspection document regarding this, customers tend not to like it when they see the shiny silver epoxy change color before their very eyes. It's viewed by many as a cosmetic defect, but still needs to be addressed. A word of caution: there may be some designs that rely on a very specific electrical conductivity of the backside Ag epoxy attach and changes in surface conductivity after blackened should be investigated. Oxidation of other exposed surfaces should also be looked at.

One common approach to reverse the blackening of the epoxy is to subject the unit to a subsequent argon plasma treatment where the surface oxides are ablated away. The result is a grayish or frosty fillet that is close, but not quite the appearance of the original fillet. Nevertheless, the blackened surface has been restored to a condition more acceptable to the customer.

A heat treatment above the glass transition temperature of the cured epoxy has also shown to restore the physical appearance of the fillet. A short time (less than an hour) at some nominal temperature, e.g. 125^{o} C seems to renew the finish of the fillet. But here the questions of chemistry start to mount up! This is where we recall that chemistry happens. And in this situation, it can be surmised that any un-reacted species within the fillet can still "bleed" to the surface. Recall that this is a continuum and the various chemical species within the fillet are still seeking a state of equilibrium. Hence, above the glass transition temperature the more mobile molecular species, although far fewer, continue to have greater mobility within the resin matrix. As they "flow" to the surface they can coat the freshly cleaned and mottled surface of the silver flake, thereby giving a more normal or shiny appearance to the fillet.

This effort is a lot more than just making the epoxy look good. It's about employing a rigorous O_2 plasma treatment prior to wirebond to super clean the devices and greatly diminish rework cycles related to wirebonding.

The final solution needed to improve wirebond yields, increase throughput and greatly reduce expensive rework cycles is a simple two step process that can be accomplished with minimal capital and disruption to the existing process flow. Step one is to inspect for resin bleed out and other organic surface contaminants and step 2 is to introduce an O_2 plasm cleaning step followed by an argon plasma and then a nominal bake, if needed. This is all done prior to wirebonding and the results will speak for themselves.

Final Remarks

Without the benefit of filtered light it's difficult to really inspect for epoxy bleed and other microscopically thin layers of surface organics. These contaminants on a bond pad greatly impede wirebonding (REF 4,5), especially for fine gold wire on a gold pad, which is the norm in the microwave industry. This leads to rework, which feeds the "Hidden Factory" and drives up cost that is hard to track. Hopefully, this white paper will encourage process/quality engineers to explore the possibility of incorporating O_2 plasma cleaning into the manufacturing flow and thereby produce more reliable products for the US military and for other high reliability applications in the commercial and medical sector.

Thomas J. Green has more than 38 years combined experience in industry/academia and the DoD. He earned a B.S from Lehigh University in Materials Engineering and an MEA from Univ of Utah. He is a recognized expert in materials and processes used to assemble hybrids, RF microwave modules/5G, Class III medical implants, optoelectronics, and other types of hermetic/non-hermetic packaged microcircuits and sensors. He has considerable expertise in hermetic testing methods per TM 1014 and moisture related failures in general. Serving as a Research Scientist at the U.S. Air Force Rome Air Development Center, Tom worked as a reliability engineer analyzing component failures and in industry he was the process engineer at Lockheed Denver. He has invaluable experience in wirebond, die attach, hermetic sealing, FA and root cause identification, For the last 18 years, Tom's expertise has helped position TJ Green Associates LLC as a recognized industry leader in teaching and consulting services for high-reliability military, space, and medical device applications. Tom is a retired military officer and a Fellow of IMAPS (International Microelectronics and Packaging Society).

Philipp wh Schuessler Mr. Schuessler completed his undergraduate and graduate academic work in Analytical and Synthetic Inorganic Chemistry in 1965. He retired from IBM/FSD and Lockheed Martin as a Senior Scientist after thirty-five years in 1996. Since then, he has done consulting for the microelectronic industries. His specialties are analytical chemistry and the failure analysis of electronic devices for DOD and NASA, as well as performing Applied R&D for the U.S. Navy and NASA in moisture permeation/standardization. In 1986, he led the IBM/FSD Challenger Shuttle Recovery Team at the Cape in Florida and in Owego, NY. , where he established new cleaning and storing concepts for the electronic and microelectronic hardware that needed to be accessed later for the data that it still retained. He organized an *ad hoc* group of technologists from across the U.S. to address the issue of hydrogen evolution and moisture formation in hermetic microelectronic devices. As a member of JEDEC, he chaired the task groups for Method 5011 (Adhesives and Polymeric Materials) and Method 1018 (Residual Gas Analysis). He has authored on various aspects of industrial chemistry, over sixty papers and published articles, twenty published invention disclosures and four published patents. He has published the book, "Moisture in Microelectronics". And has been the coordinator of the Minnowbrook Microelectronic Conference since 1985.

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