PWB Creeping Corrosion Mechanism and Mitigation Strategy

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Abstract

Immersion Silver has become increasingly popular as a PWB final finish due to the robustness of the plating process in fabrication, and the robustness of the immersion silver deposit during assembly operations. Currently Immersion Silver is being used widely for a broad variety of PWB applications. The introduction of electronics into increasingly harsh environments, in both the industrial and consumer arenas, has led to the relatively recent discovery of a corrosion phenomenon induced by exposure to humid, sulfur-bearing atmospheres. Referred to as Creeping Corrosion, this phenomenon is characterized by growth of copper sulfide crystals from copper features on the outer surfaces of the PWB. The degree of corrosion may be to the extent that electrical failures can occur. PWB process factors are examined to better understand how the Creeping Corrosion growth mechanism functions, as well as how to minimize and retard the onset of corrosion of the assembled PWB (PWA). A special test method to reproduce Creeping Corrosion is described. DOE results from process experiments utilizing certain PWB fabrication approaches, and potential improvements for the mitigation of Creeping Corrosion are discussed.

Keywords: immersion silver, creep corrosion, self assembled molecules, SAMs

Introduction

It has been well established in many previous reports by Veale [1], Mazurkiewicz [2] and Schueller [3] that creep corrosion can occur on any surface finish, some have better creep resistance, but ultimately if a circuit board is repeatedly exposed to a moist sulfur source, creep corrosion will occur. Creep corrosion is not to be confused with electrochemical migration found with thick electrolytic plated silver. Electrochemical migration failure mechanism is characterized by long dendrites that grow in one direction, typically from one electrical source to another until a bridge is formed and a short occurs. Underwriters Laboratory changed their position on immersion silver as a surface finish after industry support and data was reviewed. [4] Creep corrosion is formed when unprotected copper reacts with another metal in an acidic medium such as moisture containing sulfur. The copper sulfide crystals that form grow in all directions equally. One such example can be found in Figure 1, which shows a tree ring type formation as the circuit is exposed to repeated moisture.

Figure 1

In the figures 2 & 3, showing creep corrosion before and after removal of corrosion products, it is clear to see that copper is the feed stock for the migration. From the photo of the via hole showing corrosion products it is difficult to determine the source of the corrosion product. However from the photo of the cleaned via, it is seen that most of the silver coating is intact, and it is the copper beneath the silver that is the corrosion feedstock.

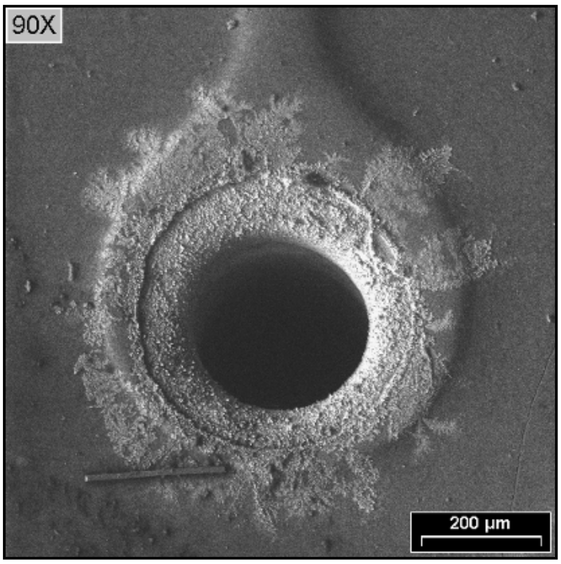


Figure 2

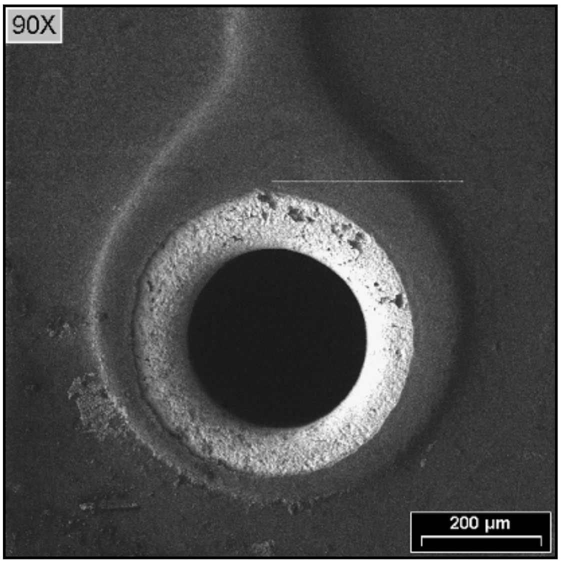


Figure 3

Failure Mechanism

On circuit boards there are two main sources of copper which need to be protected. The first source has been well documented and that is at the copper soldermask interface. In this area, copper does not exchange with silver, and in severe cases this area can become the only source of copper for reaction with the silver bath resulting in soldermask interface attack.

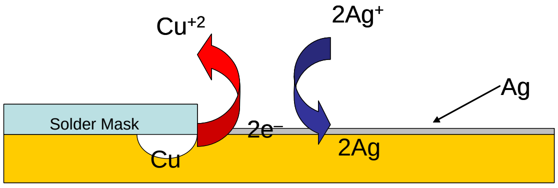


Figure 4

Typically this is best viewed by removing the soldermask altogether after silver plating, but by using a scanning electron microscope we are able to see the copper source. See Figure 5.

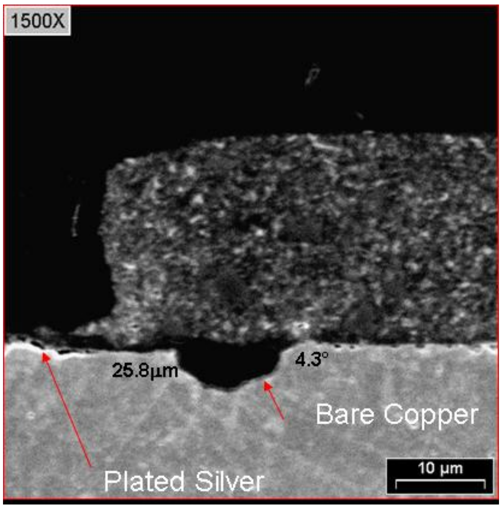
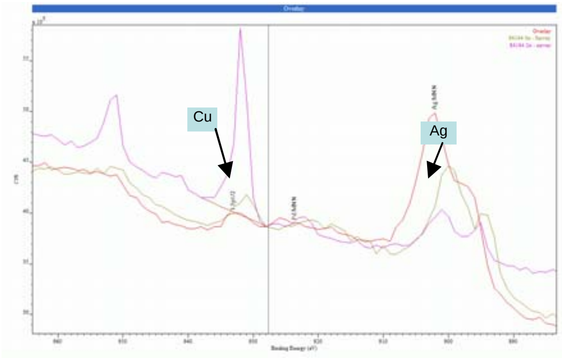


Figure 5

The second source of copper available for reaction is from the silver plating itself, or more specifically through pores in the plating. After heat cycling of circuit boards, copper migrates to the surface of the silver finish. In Figure 6 we show XPS scan of the surface of an immersion silver plated board after 0, 1 and 2 heat cycles. Without any heat cycles, the silver peak is most prominent, but after 2 heat cycles, the copper peak becomes more pronounced.



- **XPS Analysis Shows That There Is No Copper Peak (932 Ev) Before Reflow.**
  - **After 2x Reflows, The Copper Peak Increases, The Silver Peak Decreases**

Figure 6

Additional sources of copper include partially plugged via holes and thin mask which cracks under stressful conditions. When soldermask is applied to the circuit board, via holes are intentionally photo image exposed and not developed. This usually results in a soldermask cap on one side only leaving a very deep blind via hole to be plated. When a blind via hole has an aspect ratio greater then 5:1, standard horizontal plating equipment cannot properly delivery cleaning, plating or rinsing chemistry resulting in exposed copper. This bare copper becomes a ready source for reaction, especially if any acidic cleaning chemistry is left inside. Simple ionic contamination testing can help determine if a plating machine is able to effectively process partially plugged via holes. If ionic values for a bare board exceed 6.5 micro grams per square inch with immersion silver, it is quite likely the plating machine's rinsing capability is being exceeded.

Thin soldermask will also lead to exposed copper, especially after assembly. Most soldermask is screened onto circuit boards using a variety of mesh sizes. Typically the lower the mesh number, the thicker the mask will be deposited. On a perfectly flat circuit board with no topography, 1-2 mils of soldermask will be deposited. However, circuit boards do not have uniform topography, etch patterns create bumps and ridges. Unbalanced circuitry or poor plating distribution can create isolated areas of high plating resulting in thin mask. Via holes are especially susceptible to this problem. Figure 7 clearly shows creep corrosion occurring in an area designed to be protected by soldermask.

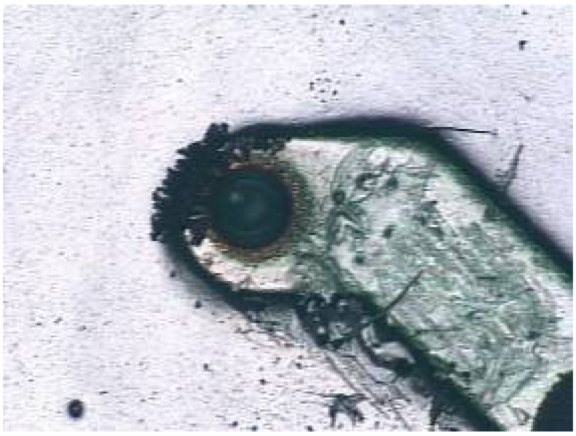
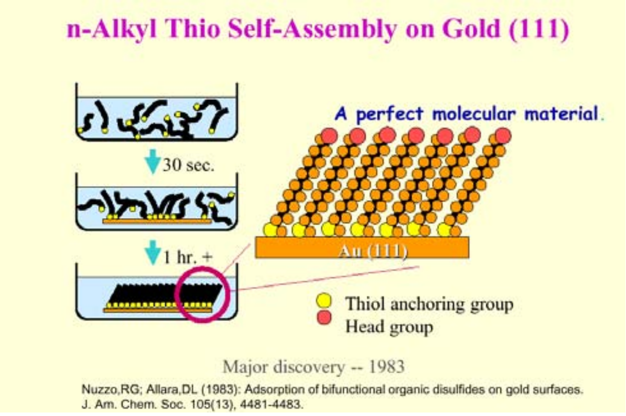


Figure 7

What could be of interest to the industry in terms of better via capping and fewer thin mask areas for less creep corrosion initiation sites is the return of dry film soldermask. This application method has fallen out of favor as liquid photoimagible solder mask became more popular, but perhaps there is still a place for this technology. If overall mask thickness can be reduced from the traditional 4 mils and costs can be reduced this technology may still have some benefits.

Self Assembled Molecules

What are Self Assembled Molecules? They are bi-functional or multi-functional molecules with two or more distinct termination groups with different functionality. Typically one end is attached to a specific surface while the other end provides a specific functionality. Self Assembled Molecules or SAMS have been known to the industry for over 25 years. SAMs were first discovered in 1983 by Nuzzo and Allara, who worked with n-Alkyl Thiol on gold plated surfaces. It was observed that this molecule would initially deposit in a random fashion to the gold surface, but with longer exposure the molecules would begin to align in a distinct fashion to create a tight matrix.



n-Alkyl Thio Self-Assembly on Gold (111)

Major discovery -- 1983

Nuzzo,RG; Allara,DL (1983): Adsorption of bifunctional organic disulfides on gold surfaces. J. Am. Chem. Soc. 105(13), 4481-4483.

Figure 8

The use of SAMS on immersion silver allow for an ultra thin, acid resistant, hydrophobic layer to deposit on the surface of the silver. [8] By creating a barrier to the copper and silver the thin organic coating provides excellent tarnish and corrosion resistance before and after heat cycling.

Test Methods

Initially our testing was greatly inhibited by the fact there was no industry standard method to predictably create creep corrosion. Initial testing relied on severe tarnish testing using a combined exposure of 120 minutes to sulfur dioxide followed by 2 minutes with hydrogen sulfide. If results looked promising, mixed flowing gas testing was used on test parts, but without predictable outcomes. Sometimes no creep was observed on either the control or the test vehicle. This approach was both time consuming and expensive with little positive progress.

Since those early days, Randy Schueller publicized his Chavant Clay method. We adapted a version of this method to reliably create corrosion. Our test makes use of 400-500 grams of clay, large desiccators, an oven, water, circuit boards and a freezer.

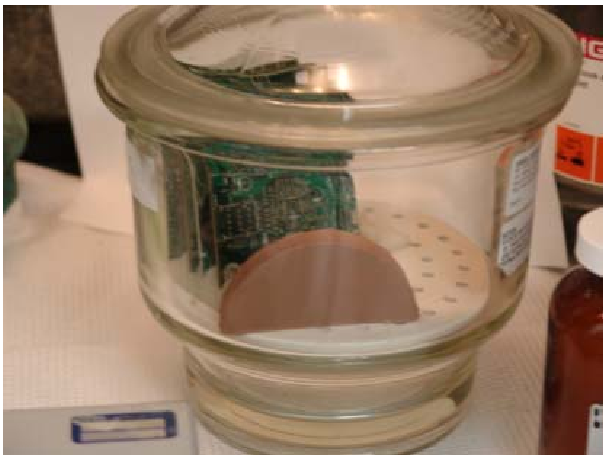


Figure 9

The clay would be moistened with water and placed in an oven at 60°C for a period of one hour to allow the chamber to become warm and the clay to emit gas. A test circuit board preconditioned with 0, 1 or 2 lead free heat cycles would then be taken from a refrigerator, placed into the desiccator and the lid replaced. The warm moist sulfur rich gas from the clay then condense on the cold circuit board. This procedure is repeated 2 times per day. Parts are inspected with 30X magnification periodically and a final inspection is performed after a period of 2 weeks and rated on their corrosion resistance.

A second method developed by a researcher at a collaborative OEM used a similar method to generate creep corrosion. The main difference of their method versus our method was the use of ammonium sulfide gas in place of the Chavant clay. The same methodology of introducing cold circuit boards into a hot moist gas is used. This test method yielded slightly different, but in general very similar results to the clay method. During separate DOE testing, both methods tended to isolate the same test coupons as good or bad, allowing for independent arrival at the same optimal parameters.

Immersion Silver Post Dip Criteria

In developing the solution for creep corrosion suppression, there were several factors involved which required consideration for the material to be successful. The material chosen needed to be applied in a cost effective manner that did not add labor or undue expense to the immersion silver operation. What has been developed is a post treatment bath based on SAMs technology that is applied in line with the silver process in 30-60 seconds.

Figure 10

Solderability was another consideration for the post treatment solution. The material could not have a negative impact on solderability. Figure 11 shows wetting balance curves on treated and untreated immersion silver coupons with and without heat cycles. No negative effect on solderability was observed.

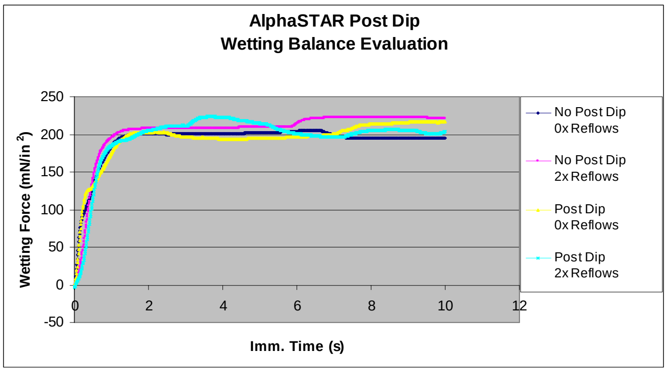


Figure 11

Thermal stability was also a critical need for long term corrosion suppression. Simple anti-tarnish molecules would not be beneficial due to low thermal degradation temperatures. The SAM molecule chosen for silver corrosion suppression has thermal stability well over 300°C, far in excess of all lead free assembly temperatures.

Contact resistance is not affected before or after heat cycling due to the ultra thin nature of SAMs. This is an added benefit for both PWB Fabricator and Assembler. See Figures 12 & 13. Fabrication houses can test post immersion silver application and not have false failure concerns. Assemblers can continue to benefit from immersion silver's historically low contact resistance for post assembly testing.

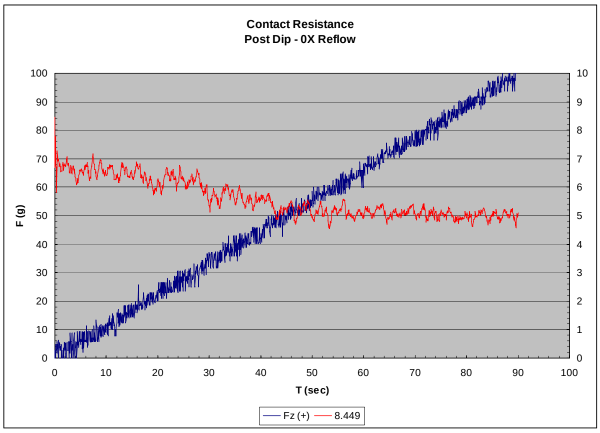


Figure 12

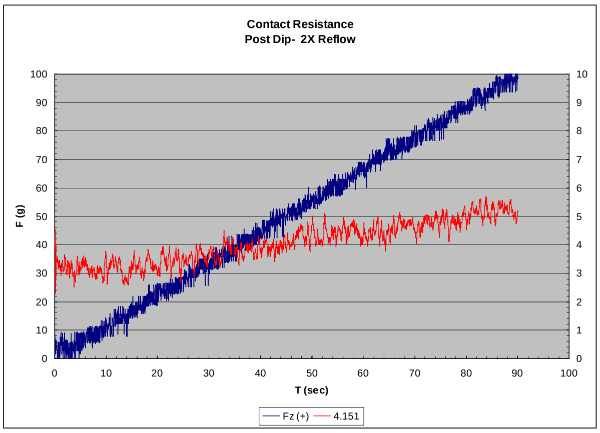


Figure 13

Creep corrosion suppression for immersion silver is the ultimate goal for a post dip. The SAM based material has proven quite effective in suppressing creep corrosion with either the clay method or the hydrogen sulfide method. In Figures 14 & 15 there are two identical circuits from the same lot code of production. Both are immersion silver plated, one has a SAM based post treatment applied, the other does not. They were both subjected to the same corrosion chamber at the same time under the same conditions.

Figure 14

Figure 15

The results of the 14 days test are clear to see.

Design of Experiments

Prior to conducting DOE's, several rounds of screening tests were performed with various post treatment molecules to determine if an existing chemical platform existed which may suppress creep corrosion. Simple benzotriazole and more complex benzimidazole were not successful in passing tarnish or corrosion testing. Early testing indicated that low etch or a non-micro etching preclean may reduce creep corrosion, but subsequent testing showed this to be a false lead. Exploration of solder mask adhesion promoters to reduce undercut were also explored under the theory less crevice would yield less exposed copper, but they ultimately proved to be ineffective.

What ultimately proved effective was the use of a novel SAMs molecule designed to bind to copper and silver and provide a hydrophilic surface.

Additional Considerations

During the course of learning the best application methods for SAM based post dip on immersion silver, it was proven assembly paste flux will also play a factor in the probability that creep corrosion will be generated on an assembly in the test chamber. Parts were assembled with two different halogen free pastes by two different paste suppliers. Both met the common "halogen free" definition in that they contained less than 900 ppm of chloride and bromide with a combined total of less then 1500 ppm. All SAM treated parts subjected to the Chavant Clay method of corrosion passed corrosion testing, but one paste exhibited corrosion failures on the component side only using the ammonium sulfide gas method. Much more work needs to be done in this area, and additional research is under way at this time.

Conclusion

Practical board design can eliminate creep corrosion in most environments with any surface finish. Designing parts to have solder mask cover as much real estate as possible is one approach. Completely filling high aspect ratio via holes with solder mask will eliminate poor rinsing and plating, which in turn leads to exposed copper and reactive sites. Using fewer mask defined features will also aid in reduction of creep corrosion initiation sites.

Several months of time was lost initially due to the lack of a predictable creep corrosion propagation method. However, once a method was developed and shared with the industry, the original hypothesis of the effectiveness of a Self Assembled Molecule based post dip was realized. A post dip utilizing Self Assembled Molecule technology offers the best hope to suppress creep corrosion at the bare board level. This applied coating has resistance against acids and isopropyl alcohol and will remain with the assembly as it goes into service.

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