Tech Talk

Fine Lines in High Yield (Part CXLI)

Ferric Chloride Etching of Copper

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Ferric chloride etching is the standard process for photochemical machining of stainless steel. Much has been published about this process and the regeneration of ferric chloride spent etchant in "The Journal" of the Photo Chemical Machining Institute (www.pcmi.org) but little has been written in recent years about the use of ferric chloride in the fabrication of PWBs. This Tech Talk column attempts to give some background on ferric chloride etching, including anecdotal information that I have collected from the industry.

The main sources of ferric chloride are steel manufacture where ferric chloride is produced from spent steel pickling solution. Another source is the production of titanium dioxide where ferric chloride is a byproduct. The major uses for ferric chloride are municipal wastewater treatment and potable water treatment where ferric hydroxide acts as a very effective flocculating agent. The use in photochemical machining and electronics is only a minor component.

The chemistry of ferric chloride etching of copper is summarized in Figure 1.

Equation (a) shows the first step in copper etching namely the oxidation of metallic copper to cuprous chloride whereby ferric chloride acts as the oxidizing agent as it is reduced to ferrous chloride. Equation (b) then shows how cuprous chloride is further oxidized by ferric chloride to yield cupric chloride. As cupric chloride builds up in the etchant, it in turn can act as an etchant as is shown in equation (c). As the concentrations of ferric chloride and cupric chloride are changing, we have two different reactions with different reaction rates and changing starting material concentrations which seems to be the reason why people who have experience with both, cupric chloride etching and ferric chloride etching report that ferric chloride etching is more difficult to control.

Equation (d) shows an undesirable side reaction, the hydrolysis of ferric chloride to ferric hydroxide and HCl. Ferric hydroxide is not very stable and will split off water to form basically rust. It is the ferric oxide/hydroxide that is mainly responsible for the staining of work pieces or anything else for that matter that comes in contact with the etchant. This staining can be minimized by shifting the

(a) $$FeCl_3 + Cu \longrightarrow FeCl_2 + CuCl$$

(b) $$FeCl_3 + CuCl \longrightarrow FeCl_2 + CuCl_2$$

(c) $$CuCl_2 + Cu \longrightarrow 2CuCl$$

(d) $$FeCl_3 + 3H_2O \rightleftarrows Fe(OH)_3 + 3HCl$$

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equilibrium of Equation (d) to the left side by the addition of HCl which is being practiced in ferric chloride etching. Ferric chloride etchant is normally replenished on-site by the addition of chlorine which converts the ferrous chloride back to ferric chloride, the active etching ingredient. As more and more copper builds up in the etchant (e.g. up to 100g/l of copper in a solution containing about 530g/l of ferric chloride)) the etch rate decreases substantially, further replenishment with chlorine makes little sense, and the spent etchant is shipped to a processor that has the ability to separate the copper and reclaim the etchant. Photochemical machining shops may use chlorine in 200 pound cylinders. PWB shops need to check local regulations regarding the use of chlorine. I remember an accident at a PWB shop in California that caused a ban of chlorine use in PWB fabrication. The shipping of such cylinders is not as problematic as the shipping of chlorine in rail road tank cars which is facing much tougher regulations in the future. To avoid chlorine shipments altogether, large chlorine users such as PVC plants are typically found right next to chlorine generating facilities. There is increasing pressure from environmental groups to reduce or even eliminate the use of chlorine completely. The electronics industry is on the way of eliminating PVC wire insulation, driven by incidents such as the devastating fire at the Duesseldorf, Germany, airport a few years back.

Ferric chloride has the reputation of giving a more favorable etch factor (less lateral etch) than cupric chloride. I don't have data to this effect, and engineers whom I talked to and who had experience with both processes in PWB fabrication did not have solid results to corroborate this, in part because equipment parameters also affect the etch factor and processes in different equipment sets are difficult to compare. It is not obvious what component in the ferric chloride etchant might act as a banking agent to protect the etched side wall of a copper feature from further lateral etching. "Dragon's Blood", a red naturally occurring resin has been used successfully to protect side walls from more lateral etching. The Bosch dry etching process may also be considered a process that makes use of a banking agent. In stainless steel etching with ferric chloride there is a naturally occurring banking agent that gives a more favorable etch factor. It is a complex, gooey, dark-colored mix of insoluble impurities for which Professor David Allen of the Cranfield University lovingly coined the term smut. It tends to build up under the photoresist overhang in the recessed area near the top of the etch channel where there is less liquid turbulence and impingement than at the more exposed lower flank and bottom of the etch channel, thus acting is a banking agent. Ferric chloride etchant with a high Baumé (e.g. 48) will cause less smut than lower Baumé etchant, but the high Baumé etchant will have a slower etch rate. Shops that prefer the cleaner, low smut etchant, and need a higher throughput have resorted to higher temperature processing which requires titanium equipment.

In Japan I found both ferric and cupric chloride etching in PWB production. CMK has practiced ferric chloride etching, controlling the process by specific gravity. Clover (in Hokkaido), if I remember correctly, used to practice ferric chloride etching but the cost and logistics of etchant recovery in this location became prohibitive. NanYa used ferric for a while but then switched. Asahi Denka markets a fine etch ferric chloride control system that includes a proprietary additive replenishment. In Taiwan, cupric chloride etching dominates but there are several shops where both ferric and cupric chloride etching is practiced (e.g. Unitech). Wus has ferric chloride etching in Taiwan but does cupric chloride etching in China. Ferric chloride etching is not common in Korea. Korea Circuit may be the only user. In the US I have seen ferric chloride etching of PWBs only at KCA, a subsidiary of Korea Circuit in California.