

# Acid Copper Plating with Insoluble Anodes - A Novel Technology in PCB Manufacturing

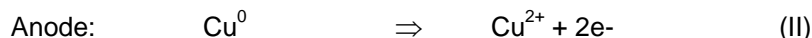
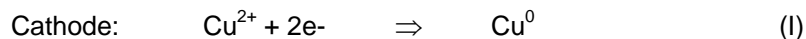
Dr. Jürgen Barthelmes  
Atotech Germany  
Erasmusstrasse 20  
D- 10553 Berlin Germany

## Short Abstract (Synopsis)

In the paper presented the novel technique of plating printed circuit boards with insoluble anodes is explained. The basic electrochemical equations of different electrolyte alternatives are shown and the advantages and disadvantages of these systems explained. A general understanding of the meaning of anode potentials, the interpretation of potential current functions, the development of the ferrous ion concentration (in the Atotech electrolyte) with time and current density and the interaction of organic additives with the new substrate is discussed. Combining insoluble anodes with pulse plating as state-of-the-art technology proves to be a most efficient tool for the production of current high end and future PCBs, including blind microvia boards of very difficult aspect ratios.

## Introduction

In the past acid Cu plating in printed circuit board (PCB) manufacturing was based on two simple, electrochemically induced reactions. While metallic copper is deposited on the PCB cathode, the reverse reaction, namely the dissolution of Cu, takes place at the anode.



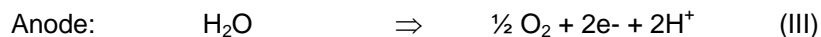
The Cu anodes for that particular application contain between 0.02 and 0.08 % of phosphorous, needed to avoid excessive polarisation during dissolution.

Cu anodes exist in a variety of shapes, ranging from bars to individual balls contained within a Titanium basket.

Since it is agreed upon that Cu deposition is needed to manufacture a PCB, one does not contemplate about alternative cathode reactions. However, as far as the processes at the anode are concerned, different approaches can be attempted. The deposition of Cu will always be the thermodynamically favoured anodic process, the system to be implemented must therefore not contain metallic Cu. The future anode has to be stable in the corresponding electrolytic environment and must remain insoluble.

## Oxygen Evolution as Anode Reaction

If any conventional acid Cu electrolyte were used with insoluble anodes, oxygen would be formed at the anode surface, resulting in the degradation of water.



The anode potential for that reaction has to be considerably higher, due to a normal potential of 1.0 V (vs. Ag/AgCl). Increased consumption of brightener and leveler components contained within the electrolyte would result. Organic reaction products are formed which may inhibit or even passivate the anode surface. The surface distribution on the PCB cathode may be influenced.

The experience with insoluble anodes working in an acid Cu electrolyte is limited even on the suppliers side. The effect of highly anodic potentials on the lifetime of the material is therefore unknown, a fact particularly interesting considering the costs for the coated anodes.

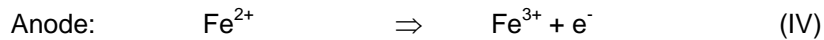
Cupric ions will have to be replenished to maintain the  $\text{Cu}^{2+}$  concentration, giving rise to an additional potential source of electrolyte contamination. For horizontal applications the  $\text{O}_2$  bubbles formed at the bottom anodes may remain on the lower side of the PCB, eventually causing surface defects.

Summary of disadvantages and possible dangers of oxygen evolution:

- ⇒ high consumption of organic additives
- ⇒ decreased anode lifetime
- ⇒ potential passivation by organic reaction products
- ⇒ replenished  $\text{Cu}^{2+}$  ions a contamination source
- ⇒ oxygen bubbles causing surface defects on PCB

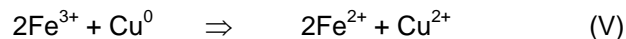
### The Atotech Approach

In order to keep the anode potential low during the plating process, an alternative reaction to oxygen evolution has to take place. For applications with insoluble anodes Atotech electrolytes therefore contain a sufficient amount of ferrous ions as to completely draw the electrons needed for the anode reaction from the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ .



Due to the normal potential of reaction IV (+ 0.55 V vs. Ag/AgCl) the anode potentials remain very low. As a result the consumption of organics is not only comparable, but substantially reduced to less than 50 % of the values for conventional plating. Lifetime issues and passivation effects are less likely to occur.

If  $\text{Fe}^{2+}$  is sufficiently high, the amount of  $\text{Fe}^{3+}$  formed in the plating cell per unit of time is a function of applied current density only. The  $\text{Fe}^{3+}$  containing electrolyte is pumped into an external module (and back) containing electrolytic Cu metal which is stripped via the reaction of



Through this chemical process, which takes place in the so called replenishment cell,  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  are maintained within the entire system.

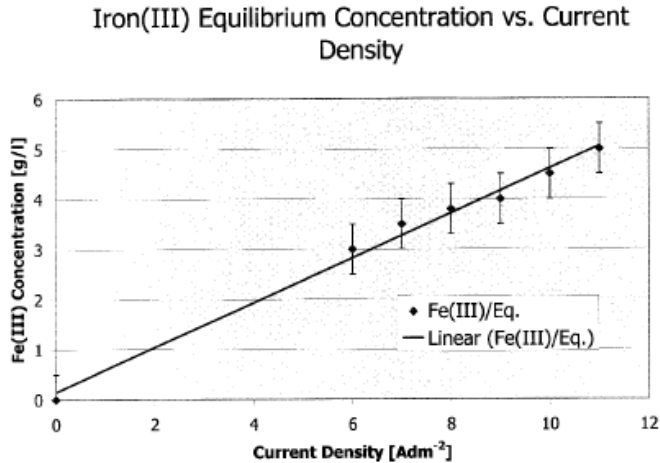
The anode reaction (IV) in the plating cell constitutes the source of  $\text{Fe}^{3+}$ . An equilibrium  $\text{Fe}^{3+}$  - concentration is reached when the reduction (sink) of ferric ions (V) is as high as the oxidation of ferrous ions at the anode (IV):

$$\left[ \frac{d[\text{Fe}^{3+}]}{dt} \right]_{\text{sink}} = - \left[ \frac{d[\text{Fe}^{3+}]}{dt} \right]_{\text{source}}$$

Since  $\left[ \frac{d[\text{Fe}^{3+}]}{dt} \right]_{\text{source}}$  is a function of current density  
(CD) applied the equilibrium

$\text{Fe}^{3+}$  concentration,  $[\text{Fe}^{3+}]_{\text{eq}}$ , varies: The following graph (Figure 1) for  $[\text{Fe}^{3+}]_{\text{eq}}$  vs. CD gives values obtained from production sites.

The variance found for the individual  $[\text{Fe}^{3+}]_{\text{eq}}$  values exists due to the influence of two other important factors, the Cu surface area exposed to the electrolyte and the relative velocity of the solution across the replenishment module. The former depends on Cu nugget size and the level of filling of the Cu dissolution tank, the latter on the pump rate between plating and replenishment units.



**Fig. 1: Equilibrium Fe(III) concentration versus Current Density**

### Cyclic Voltammetry and Current Efficiency

It was just explained that - besides a particularly designed organic additive system - Atotech electrolytes for applications with insoluble anodes contain the two additional inorganic species Fe<sup>2+</sup> and Fe<sup>3+</sup> in noticeable concentrations. A schematic representation of the characteristic potentiostatic current potential function, a cyclic voltammogram (CV), is given in Figure 2.

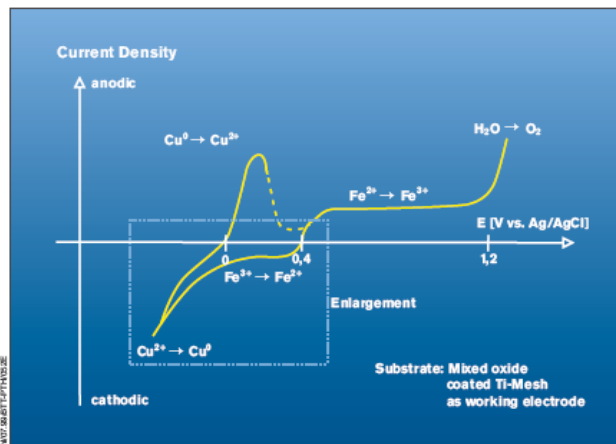
No distinct qualitative difference in the CV can be found between Cu and insoluble anode material as the working electrode. The following electrochemical processes can be distinguished at the indicated potentials. The reference electrode is a Ag/AgCl electrode. All potentials are quoted with respect to that system.

O <sub>2</sub> evolution from H <sub>2</sub> O degradation	1.2 V and higher
Fe <sup>2+</sup> ⇒ Fe <sup>3+</sup> oxidation	0.4 V and higher
Fe <sup>3+</sup> ⇒ Fe <sup>2+</sup> reduction	0.4 V and lower
Cu <sup>2+</sup> ⇒ Cu <sup>0</sup> deposition	0 V and lower

One can see that the anode potential should be between 0.4 V and 1.2 V if Fe<sup>2+</sup> is sufficient to avoid oxygen evolution. The cathode potential will be lower than 0 V.

### Cyclic Voltammetry on Electrolyte

Applications with Insoluble Anodes  
(Potential-Current Response)



**Fig. 2: Cyclic Voltammogram of an Electrolyte for Applications with Insoluble Anodes**

## Cyclic Voltammetry on Electrolyte

### Current Efficiency for Applications with Insoluble Anodes

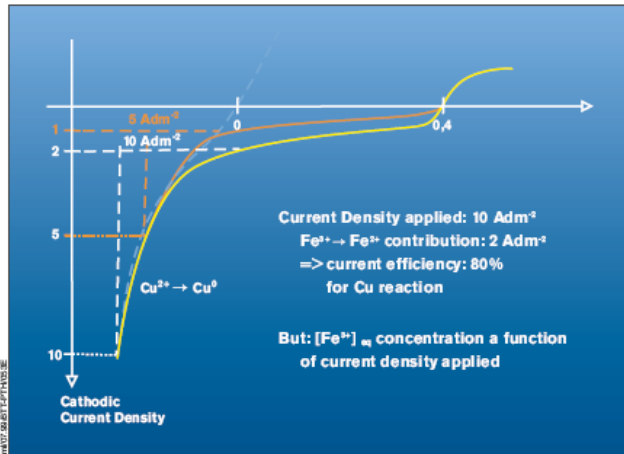


Fig. 3: Enlargement of Current-Potential Response for different Fe(III) concentrations

Both values are a function of current density and shift to more anodic (at the anode) or cathodic (at the cathode) polarizations with increased loading.

Looking at the cathodic reactions it is found that during Cu deposition on the PCB,  $\text{Fe}^{3+}$  is reduced to  $\text{Fe}^{2+}$  as well, thereby diminishing the current efficiency (CE) to less than 100%. The efficiency is a function of current density and  $\text{Fe}^{3+}$ .

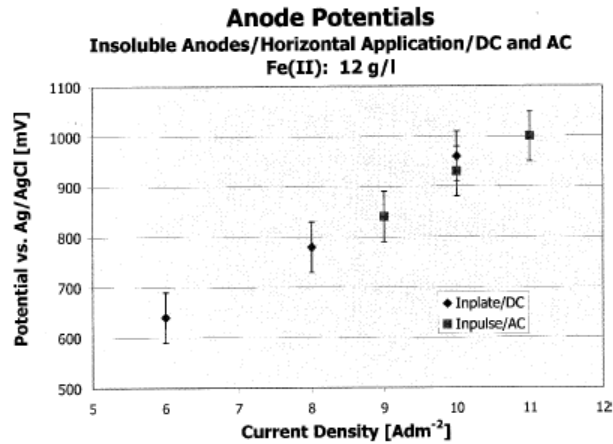
An increased ferric ion concentration leads to an increased contribution of the diffusion limiting current from the  $\text{Fe}^{3+}$  reduction to the overall current. For a given applied CD the CE for the Cu reaction can be estimated if the diffusion current for the  $\text{Fe}^{3+}$  reduction is extrapolated to more cathodic values. This is explained in Fig. 3.

For a given CD (here  $10 \text{ Adm}^{-2}$ ) a cathode potential results (here around -250 mV vs. Ag/AgCl), which determines the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  contribution (here 2  $\text{Adm}^{-2}$ ) to the overall current and most straightforward leads to the current efficiency (here 80%).

The CE is a function of CD, increasing with higher current loading. However the effect is less pronounced, since with increasing/decreasing the CD, higher/lower  $\text{Fe}^{3+}$  concentrations result, thereby changing the absolute diffusion limited current of the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  reduction. Typically the CE ranges between more than 90% ( $10 \text{ Adm}^{-2}$  and higher) to approx. 80% at  $4 \text{ Adm}^{-2}$ .

### Anode Potentials from Production Sites

Anode potentials are the most important measure to determine the sufficient amount of  $\text{Fe}^{2+}$  needed for a given current density. The potential should always remain in the region of  $\text{Fe}^{2+}$  oxidation (below 1.2 V vs. Ag/AgCl). Atotech horizontal electrolytes generally run on at least 12 g/l Fe(II). The data presented in Fig. 4 shows different anode potentials measured for Inplate (DC) and Inpulse (Pulse Plating) applications at various current densities.

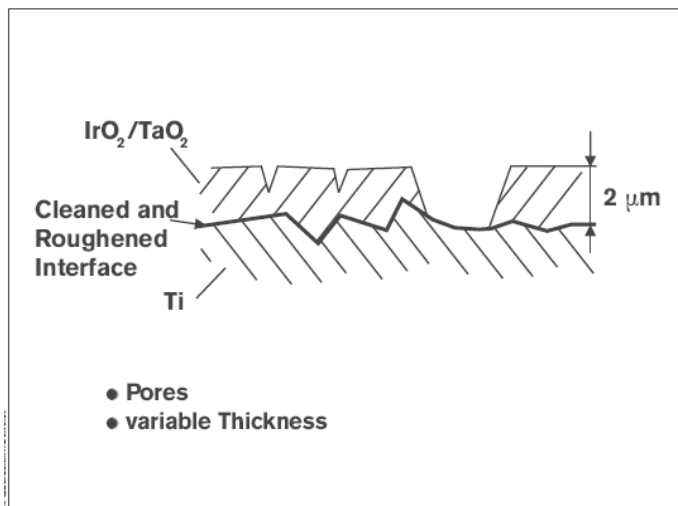


**Fig. 4: Anode Potentials as a Function of Current Density**

Even at 11 Adm<sup>-2</sup> the anode potential is below 1.2 V, indicating that oxygen evolution does not occur.

### Insoluble Anodes

#### Cross Section



**Fig. 5: Cross Section of an Insoluble Anode**

#### Morphology and Constitution of Insoluble Anodes

The insoluble anode material contains a Ti mesh as the base core which is coated with a mixed metal oxide layer of tantalum and iridium. A schematic cross section of such a material is depicted in Fig. 5.

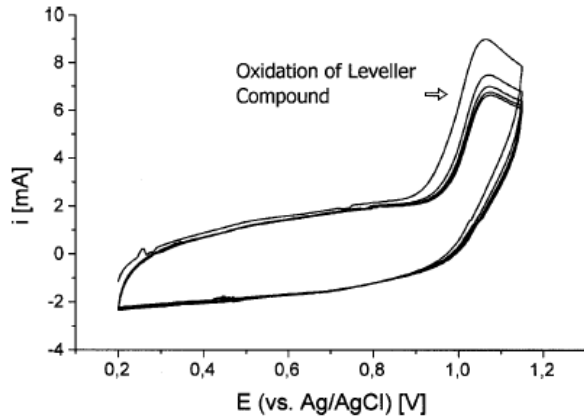
On the surface one can observe a "mud-like" morphology of the mixed oxide coating. This morphology is desired due to the increase of effective anode area. The mud chasms are sometimes as deep as the coating itself, which is between 1 to 5 mm thick, bare Ti is thereby exposed. Completely uncovered areas can also be found.

#### Interaction of Organic Components with Insoluble Anodes

##### - Chronopotentiometry and Atomic Force Microscopy (AFM) -

Cyclic voltammetric studies were performed on all of the potential additives for insoluble anode applications. In most cases no Faraday currents were detected in the range of Fe<sup>2+</sup>-oxidation,

beginning at 0.4 V up to an anodic potential of rigid oxygen evolution (1.4 V). Some leveller compounds however are being oxidized electrochemically, as can be seen in Fig. 6. The corresponding CVs indicate that - without sufficient  $\text{Fe}^{2+}$  being supplied and transported to the anode surface - these particular molecules would be consumed considerably.

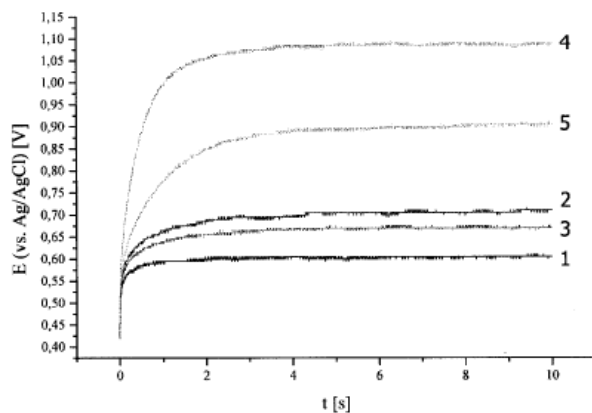


**Fig. 6: Cyclic Voltammogram of a Leveller Component being Oxidized at 1.0 V**

Chronopotentiometric investigations are to be carried out with the additives oxidized at potentials more cathodic than the oxygen evolution potential. The influence of the electrochemical reaction products on the anode performance will thereby be determined.

The following Fig. 7 shows various potential time functions illustrating that a given component partially passivates the insoluble anode working electrode after it was being loaded with potentials higher than 1.2 V. At these polarizations the component is being oxidized. In all experiments displayed the current density applied was held constant.

One can see that in order to drive the current across the cell more positive anode potentials are needed after anodic loading (curves 2 and 4). By oxidizing the additive the electrochemically active electrode surface is being reduced. Loading the working electrode with less anodic polarization partially regenerates the mixed oxide coated substrate, less positive potentials result (curves 3 and 5).



**Fig. 7: Chronopotentiometry on a Leveller**

### Component Causing Partial Passivation when Anodically Oxidized

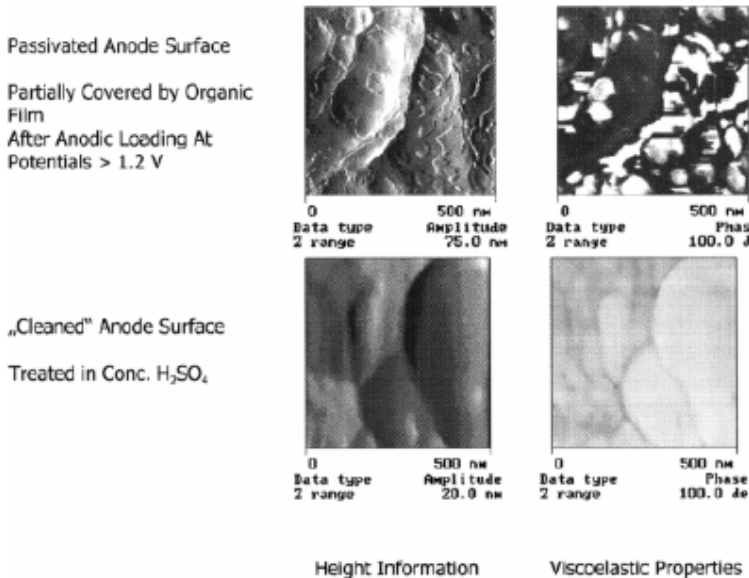
The conditions for the five experiments displayed in Fig. 7 are summarized below:

General: Chronopotentiometry at 0.025 A  
[Fe<sup>2+</sup>] : 15 g/l  
T: 298 K

#### Sequence

- curve 1: no highly anodic loading
- 2: after 1 min. at 0.06 A and 1.2 - 15 V
- 3: after another 30 min. at 0.025 A and 0.65 V
- 4: after another 15 min. at 0.06 A and 1.3 - 1.65 V
- 5: after another 30 min. at 0.025 A and decreasing to 0.8 V

A partially passivated anode can also be regenerated by cleaning the substrate in concentrated sulfuric acid. The following four pictures in Fig. 8 show the data (obtained by Atomic Force Microscopy, AFM) of a passivated (top row) and a cleaned and regenerated anode (bottom row). The left column displays the morphology (differences in heights), whereas the right column indicates the viscoelastic properties of the substrate, information about the softness and hardness of the material investigated.



**Fig. 8: Atomic Force Microscopy on Passivated and Cleaned Insoluble Anode**

From the height information one can not distinguish the passivated from the non-passivated electrode. However from the differences in contrast observed when screening the substrate in the viscoelastic mode of the AFM one gathers that a partially inhibited anode (top right) has soft (dark) and hard (bright) areas. It is interpreted that a soft organic film was deposited during the period of highly anodic loading; that particular film is then being cleaned off the surface by treating the sample with conc. H<sub>2</sub>SO<sub>4</sub> (bottom right).

This interpretation is in complete agreement with the chronopotentiometric measurements described before. It is shown that some organic additives may potentially inhibit and passivate an insoluble anode surface by film formation due to high anodic potentials; a situation which may arise if oxygen evolution at the insoluble electrodes occurs.

With sufficient supply of  $\text{Fe}^{2+}$  anode potentials will always be kept at more negative values, preventing the anode from being passivated.

### **Advantages of Working With Insoluble Anodes**

As already mentioned the  $\text{Cu}^{2+}$  to be replenished results from stripping metallic Cu pellets, which do not contain any phosphorous. The formation of sludge is strongly reduced and occurs in a module separated from the plating cell. Possible sludge is prevented from entering the plating cell by a filtration unit. No roughness or nodules are formed on the PCB. Improved yields, especially important for fine line applications, are achieved.

Anode maintenance is most easy, filling of the replenishment tank can be done during production, decreasing the machine down-times and increasing productivity. Phosphorous containing copper is somewhat more expensive than electrolytic Cu, resulting in reduced costs.

The condition of the anode does not vary with plating time; a constant anode status guarantees constant production results.

The coated Ti mesh can be distributed uniformly on both sides of the PCB cathode. An excellent surface distribution is obtained.

Due to that fact lower anode-cathode distances seem possible, particularly important in space constrained environments.

Summary of general advantages

- ⇒ very easy "anode" maintenance
- ⇒ lower costs for Cu
- ⇒ constant anode conditions
- ⇒ excellent surface distribution
- ⇒ lower anode-cathode distances possible

When using the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  auxiliary redox system further considerations are important.

The metallic Cu to be dissolved may or should be phosphorous-free. Copper obtained from recycling Cu etchants may be used to fill the replenishment tank. Thereby the loop of Cu consumption inside a PCB production is being closed.

In the presence of large amounts of  $\text{Fe}^{2+}$ , low anode potentials presumably lead to an increased anode life-time.

No danger of passivating organic films formed by anodic oxidation of electrolyte additives. Consumption of all additives is decreased, improving the long term performance of the electrolyte, due to less degradation products.

Summary of additional advantages with  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox system

- ⇒ closed Cu recycling loop possible
- ⇒ increased anode life-time
- ⇒ no passivating organic films
- ⇒ very low consumption, less degradation products

### **Different Applications - Microvia Production**

Horizontal acid Cu plating modules equipped with insoluble anodes can either run on direct current or under pulse plating conditions. The former application is called Inplate, the latter Inpulse.

The current density applied in these systems are a function of boards thickness and range between

Inplate	4 - 10 $\text{Adm}^{-2}$
Inpulse	4 - 12 $\text{Adm}^{-2}$ .

However larger current densities for Inpulse seem possible.

Inpulse in particular combines many advantages needed for the manufacturing of most advanced PCBs. No anode sludge and an excellent surface distribution combined with superior throwing power at high current densities are an excellent combination for the production of blind microvia (BMV) boards.

Currently difficult BMV dimensions have an aspect ratio of 1:1 (width/depth). Future technologies range from boards with high aspect ratio BMVs (<1:1), with three and two mil BMV diameter to those with stacked BMVs.

The following Figures 9-11 demonstrate the enormous capability of the Inpulse technique in producing PCB of the future. Comparing the current densities applied in current BMV manufacturing of comparably easy dimensions, the results are most stunning. The microsections were taken from boards entirely processed in a production environment.

Fig. 9-11: Cross Sections of Microvias from Production Sites

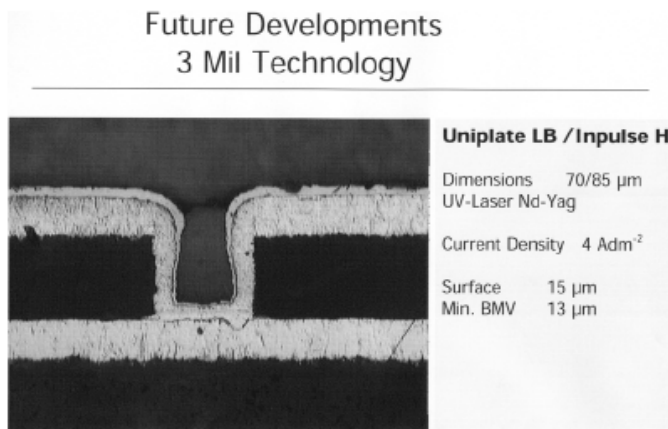


Fig. 9: Three mil Technology

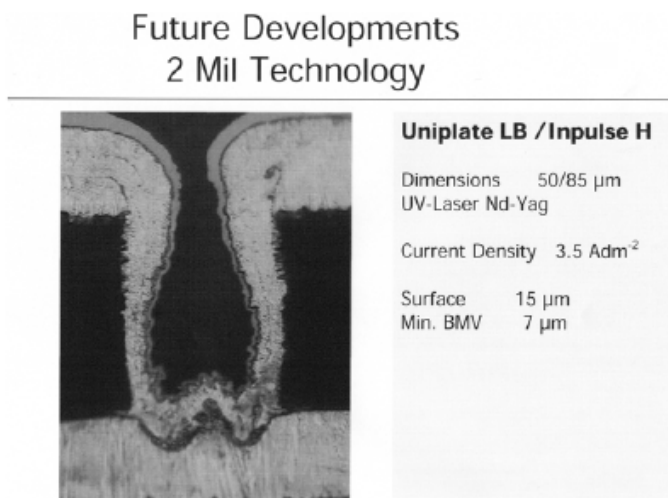
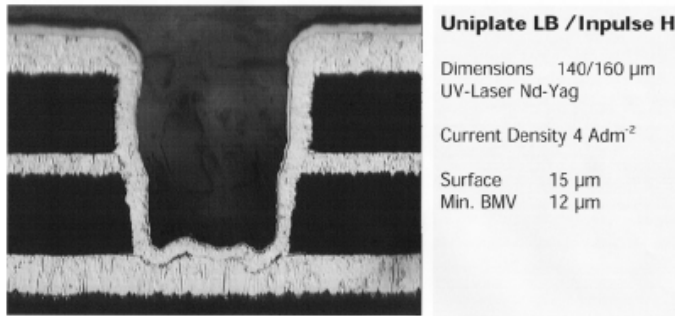


Fig. 10: Two mil Technology

## Future Developments Stacked Blind Microvias



**Fig. 11: Stacked Blind Microvia Summary**

Acid copper plating with insoluble anodes is a comparably novel technique in PCB manufacturing. However the first plating systems were put into production already two years ago. Since that day an enormous amount of information and experience was gathered at the production sites as well as in the laboratories. More scientific data includes cyclic voltammetry, chronopotentiometry and Atomic Force Microscopy, more applied measurements from PCB manufacturers acquired anode potentials, current efficiencies and equilibrium  $\text{Fe}^{3+}$  concentrations. The advantages of insoluble anodes are manifold, making it most likely the technique of the future. A glimpse of the time to come is envisioned when looking at the microvia cross sections presented.

### **Acknowledgements**

The people involved in maturing the concept of insoluble anodes and in turning it into a success are so numerous, making it impossible to mention all of them. One would probably forget one or two of these individuals, who then - with all the right there is - would feel omitted. This needs to be avoided under any circumstances!

### **About the author:**

Dr. Jurgen Barthelmes completed his masters and Ph.D. in Physical Chemistry. His research work focussed on the adsorption of organic molecules on noble metal electrodes, including Copper. His career at Atotech began as a technician involved in product support and R&D of plating processes. After heading the technology development team in the panel/pattern plating group he recently became product manager for PTH processes.