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Short Communication

Improved Electroless Copper Coverage at Low Catalyst Concentrations and Reduced Plating Temperatures enabled by Low Frequency Ultrasound

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Electroless Copper plating is a critical process in printed circuit board (PCB) manufacture where it is employed to make the through holes and vias of a PCB conductive for subsequent electroplating. The most important pre-treatment step before Electroless Copper plating is the catalyst solution where palladium is deposited on the surface of the substrate to initiate the plating reaction. However palladium is a critical raw material and the most expensive part of the Electroless Copper process. Therefore it would be beneficial if methods to reduce the amount of palladium used in the catalyst could be found without affecting the subsequent quality of the Electroless Copper deposit, particularly with respect to plating coverage. In this paper it is shown that the use of low frequency (40 kHz) ultrasound can enable the employment of a catalyst solution containing half the concentration of palladium typically used in PCB manufacture. This was achieved without any loss in coverage (as determined by backlight and SEM) even when lower temperature Electroless Copper plating was utilised. It is proposed that ultrasound can improve Electroless Copper coverage due to modification of the deposit grain structure rather than increased plating rates.

Keywords: Electroless Copper, Printed Circuit Board, Ultrasound, Palladium, Coverage

1. INTRODUCTION

Electroless Copper plating is an important industrial process as it enables the metallisation of non-conductive materials. For this reason it is an ubiquitous process in the electronics sector. Catalysed electroless copper metallisation is employed in Radio Frequency Identification (RFID)/printed electronics [1], Moulded Interconnect Devices (MID) [2], EMI/RFI shielding [3] and

in Printed Circuit Board (PCB) manufacture [4]. It has been used in this latter application for well over 40 years where it enables the metallisation of through holes and vias.

When electroless copper plating is utilized for the coating of non-conductive materials the substrate must first be catalysed or activated. Typically this is achieved by functionalising the material and then immersing it in a Pd/Sn colloidal solution. The Sn 'shell' is subsequently removed in either an accelerator or in the electroless copper solution itself (known as 'self-accelerating) leaving Pd nanoparticles on the surface of the material which will initiate the electroless copper deposition reaction.

A very simplified schematic of the process is shown in Figure 1.

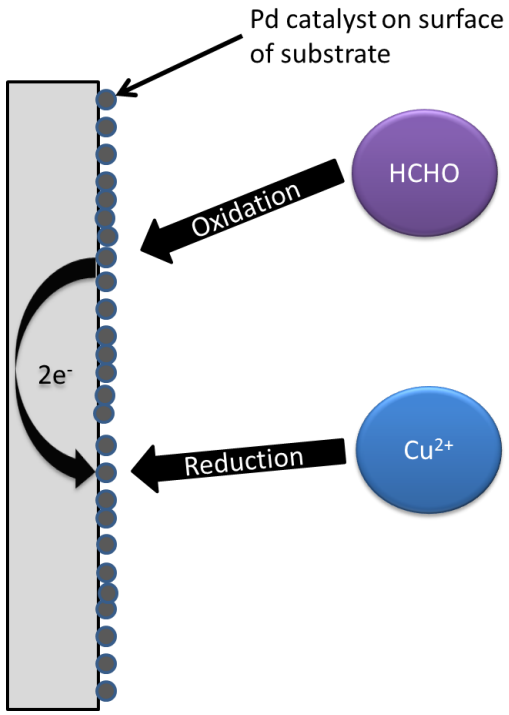


Figure 1. Schematic showing Electroless Copper reaction on a catalysed substrate (HCHO = Formaldehyde)

The amount of Pd nanoparticles deposited on the substrate surface is therefore critical to achieve fast initiation of the plating reaction, good plating rates and acceptable coverage. Indeed, achieving excellent plating coverage is becoming ever more important with the drive towards electronics miniaturisation and the manufacture of more complex High Density Interconnect (HDI) boards with very small features, holes and vias. However, the catalyst solution is the most expensive part of the electroless process due to the high cost of Pd and, being a Platinum Group Metal (PGM), it has also been identified as a critical raw material by the European Commison (http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/crm-report-on-critical-raw-materials_en.pdf). Therefore reducing the Pd required for catalysation would have major benefits for the wide range of industrial sectors which use this process and the PCB industry specifically.

Another important factor for effective electroless copper deposition is the temperature of the plating solution. Generally this ranges from 30-50 ºC but with the increased cost of energy and water it would be beneficial if electroless copper processes could be operated effectively at the lower end of this temperature scale without loss of plating quality.

The application of an ultrasonic field has been shown to have beneficial effects on electrochemical processes in general [5] and electroless copper plating in particular [6]. A recent review of the effect of ultrasound on electroless plating [7] has shown that improvements in plating rate, coverage and a reduction in porosity can be achieved.

In this investigation the effect of low frequency (40 kHz) ultrasound on the coverage of electroless copper deposits at reduced plating temperatures and lower catalyst concentrations was evaluated by determining plating rates and examining the electroless copper deposition in the through holes of PCBs.

2. EXPERIMENTAL

For all experiments a commercial Electroless Copper process obtained from Chestech Ltd was used and the general process flow is shown in Table 1. All of the solutions were made up according to the procedures detailed in the product data sheets except the Catalyst which was made up at half the recommended strength i.e. 1.5% v/v (equivalent to a Pd concentration of 0.3 g/L) and the Electroless Copper process temperature was varied between 25-50 ºC.

Table 1. Electroless Copper Pre-Treatment and Plating Conditions

Product Name	Temperature (ºC)	Time (minutes)
Circuposit Conditioner 3323A	50	5
Water rinse	Ambient	4
Circuposit Catalyst Pre-dip 3340	25	1
Circuposit Catalyst 3344 (Half Strength)	40	5
Water rinse	Ambient	4
Circuposit Electroless Copper 3350-1	25-50	25

The ultrasonic bath that was employed to sonicate the Electroless Copper was a Langford Ultrasonic, Model 375TT with a nominal operating frequency of 40 kHz. To get an indication of the ultrasonic power transferred to the solution calorimetry [8] was performed using water in place of the process solutions. Using this method the average ultrasonic intensity was determined to be 103 W/L.

Ultrasound was utilised in 2 modes.

(i) Continuous Ultrasound – the Electroless Copper solution was ultrasonically irradiated for 25 minutes.

(ii) 'Delay time' Ultrasound - the ultrasonic bath was only turned on after a 7 minute delay (7 minute stirring, 18 minutes ultrasound)

When ultrasound was not employed (referred to as 'silent' conditions) the Electroless Copper solution agitation occurred using a magnetic stirrer.

2.1. Electroless Copper Plating Rates and Deposit Morphology

The Electroless Copper plating rate was determined by the 'weight gain' method whereby test coupons of a bare PCB laminate material (Isola Duraver 104) with dimensions 2.5 cm X 2.5 cm were first dried in an oven at 120 ºC for 24 hours and weighed. They were then coated with copper using the Electroless Copper process detailed in Table 1 with each process stage being performed in a beaker containing 1 L of solution. The coupons were then dried at 120 ºC for 24 hours and weighed again. The plating rate could then be calculated from the weight gain from the equation:

$$t = \frac{\Delta m}{A\rho}$$

where t = thickness of deposit, Δm = weight gain due to electroless deposition, A= area of plated coupon and ρ = density of plated metal (copper).

The plating rates quoted in this paper are the mean of 4 coupons.

2.2. Electroless Copper Coverage (Backlight)

The backlight test is widely used in the PCB industry and has been fully described in a previous paper [9]. It enables the coverage of the electroless copper plating in the through holes of a PCB to be assessed. In many respects, as far as PCB through hole plating is concerned, this is the most important quality control check as the primary function of the electroless copper coating is to provide a conductive layer for subsequent electroplating. As long as this layer fully covers the walls of the through hole and is conductive the thickness of the deposit is not really important although, in traditional PCB manufacture, most companies that plate PCB through holes aim for around 2 μm of copper as this normally ensures the required coverage and conductivity. To determine the coverage a desmeared [10] (the desmear process cleans and textures the through holes of PCBs) copper clad FR4 multi-layer board (MLB) was used with a thickness of 1.8 mm and hole diameters of 1.0 mm. After Electroless Copper plating the through holes of this test coupon were sectioned and then examined using an optical microscope on 'backlight' i.e. the light source of the microscope was shone through the back of the sectioned holes. If the holes are completely coated with electroless copper then no light will appear and the coupon is graded as '5'. If no copper has been plated in the through hole all the light will come through and it will be graded '0'. The backlight grades recorded are the mean of 10 'through holes'. The backlight coupons were also analysed using Scanning Electron Microscopy (SEM).

3. RESULTS AND DISCUSSION

The plating rates obtained at various temperatures under 'silent' conditions with half strength (1.5% v/v) catalyst are shown in Figure 2.

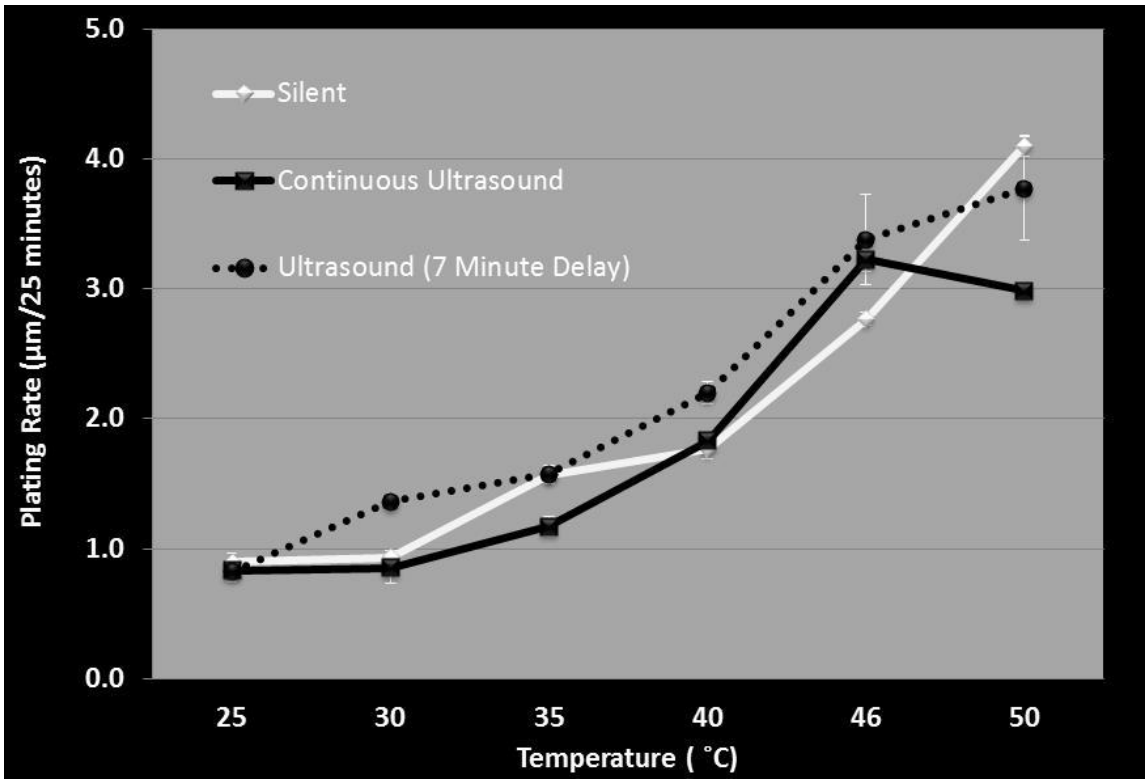


Figure 2. Effect of applying continuous and 'delay time' ultrasound on electroless copper plating rates using a 1.5% v/v catalyst

As would be expected, Figures 2 illustrates that an increase plating temperature results in higher plating rates. It is also apparent that generally the highest plating rates occur under conditions where a 'delay' time is introduced before sonication commences and that when continuous ultrasonic irradiation occurs a drop in plating rate often occurs compared to 'silent' conditions. This effect has been described in an earlier paper by the authors [11] although this previous study employed a 3% v/v (i.e. full strength) catalyst. The effect of the 'delay time' can be explained by considering the phenomenon of acoustic cavitation that occurs when ultrasound is applied to a liquid medium. Under such conditions, cavitation bubbles are formed which, when near a solid surface, collapse asymmetrically to produce microjets [12] that can hit the surface at very high speeds. These microjets hitting the surface can have a 'scrubbing' action and indeed this is the driving force behind ultrasonic cleaning. When a catalysed substrate is placed in the electroless copper solution and continuous ultrasound is employed microjets will scrub the surface removing the Pd catalyst. Figure 3 shows this effect schematically.

If a ‘delay time’ is utilised before ultrasound is turned on then this enables the catalyst to initiate the electroless reaction and then, when sonication begins, the benefits of applying ultrasound to an electrochemical system can be fully realised.

Considering the backlight results for standard (silent) agitation (Figure 4) there is a general trend for the backlight to increase as the temperature is raised. One would assume, considering the plating thicknesses shown in Figure 2, that this improvement in coverage with electroless solution temperature was due to the copper deposit getting thicker. The backlight results obtained when ultrasound was applied show a very different trend however.

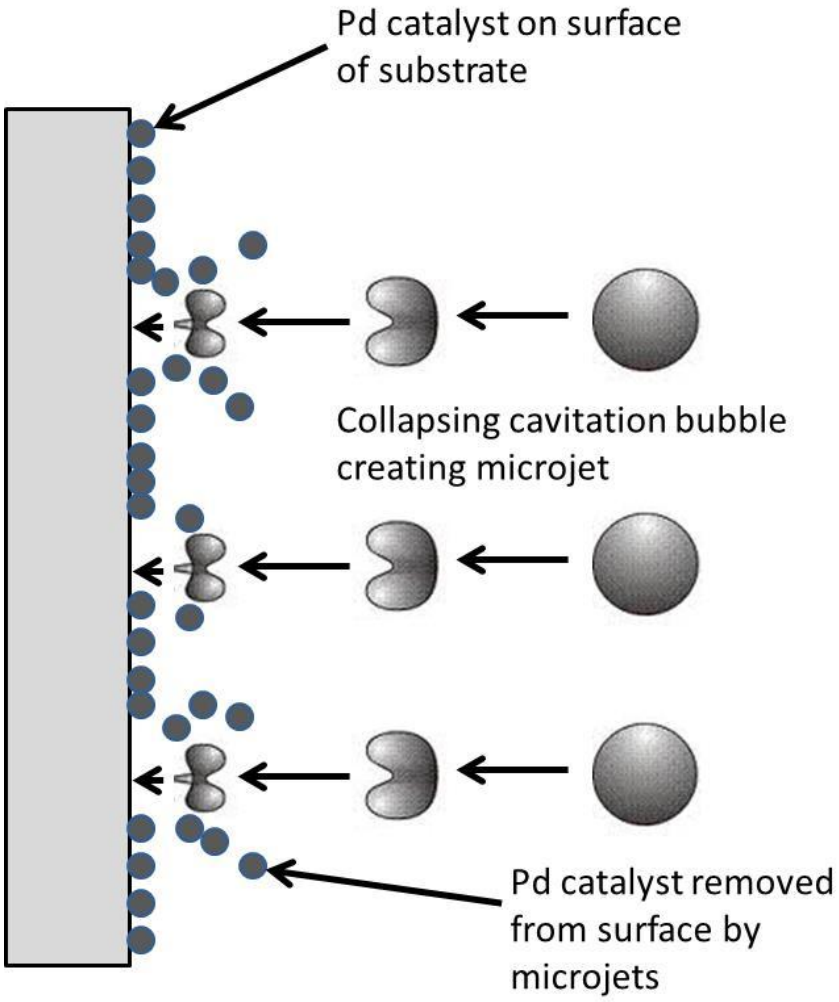


Figure 3. Schematic showing ultrasonically induced microjetting ‘scrubbing’ Pd catalyst from the surface of substrate

In this case the electroless copper coverage remained fairly constant regardless of the plating solution temperature despite the fact that the plating rate values (Figure 2) indicated that the copper thickness increased significantly with electrolyte temperature and suggests that the improvement in backlight is not due to the copper thickness deposited. This is a highly important result as it implies

that applying ultrasound during electroless copper plating could enable excellent coverage at much reduced temperatures. This effect is further emphasised in the SEM images of Figure 5 which shows the coverage of through holes in a PCB plated at 25 ºC. It is quite obvious that if conventional (silent) agitation is utilised (Figure 5a) then there are large areas of the horizontal glass fibres which have not been coated with copper. In contrast, when electroless copper plating was performed in an ultrasonic field (Figure 5b) full coverage of the through hole is apparent.

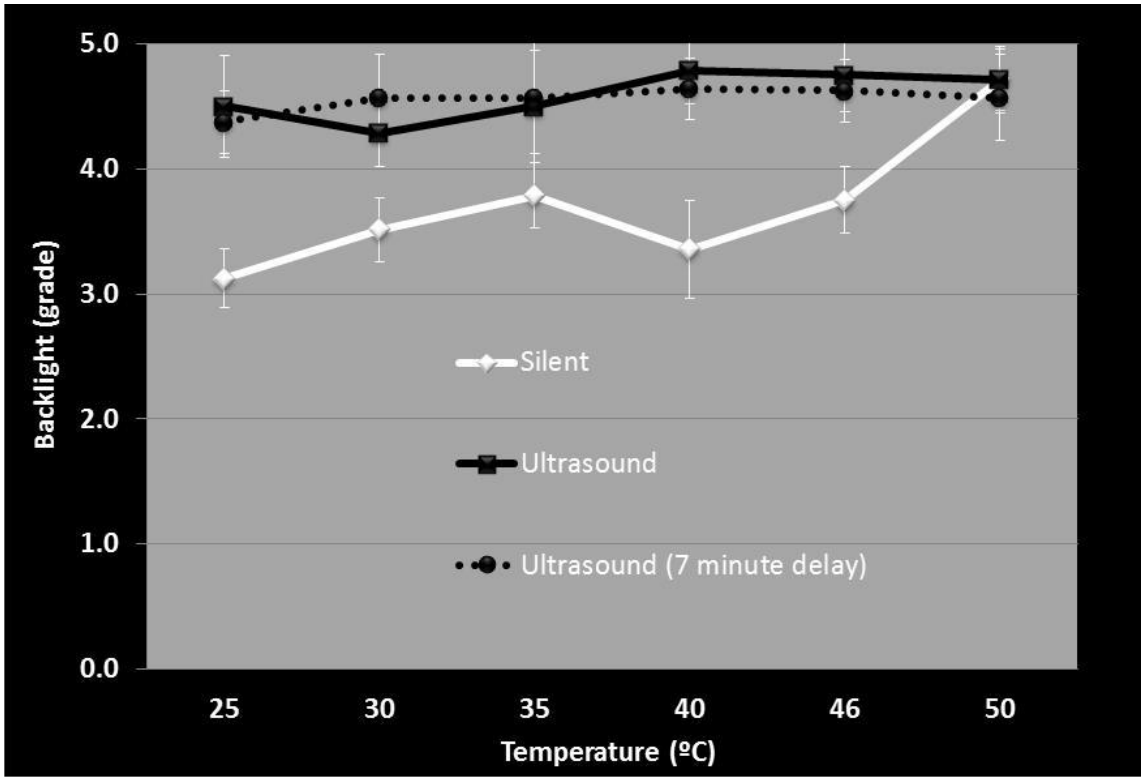
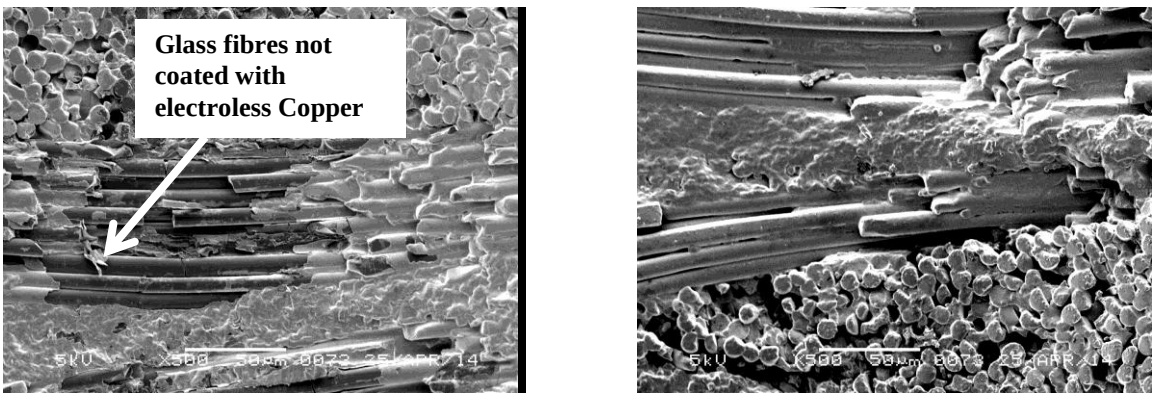


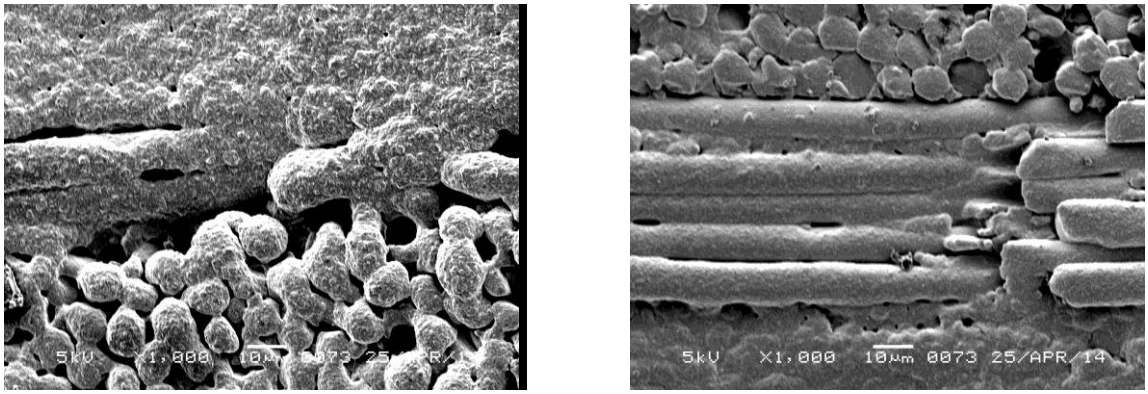
Figure 4. Effect of applying continuous and 'delay time' ultrasound on electroless copper coverage using a 1.5 % v/v catalyst



(a) Silent (b) Continuous ultrasound

Figure 5. SEM of 'through hole of PCB after Electroless Copper plating. Electrolyte temperature 25 ºC.

There are a number of possible explanations for this result. It has been previously proposed that applying ultrasound to an electroless copper plating process will result in a finer grain structure [13] with reduced porosity. The SEM images shown in Figure 6 clearly show that electroless copper deposit obtained using conventional agitation (Figure 6a) appears much coarser grained than if the electroless solution is sonicated (Figure 6b). One would expect this to lead to lower porosity and enhanced coverage.



(a) Silent (b) Continuous ultrasound

Figure 6. Electroless Copper deposit structure in through holes of PCB. Electrolyte temperature 50 ºC

The second reason for the improved coverage is that at these reduced catalyst concentrations and at lower plating temperatures the plating process is close to its operating limits and becomes more sensitive to factors such as mass transport, solution flow and the concentration of Pd on the surfaces to be plated. These factors are even more critical when Electroless Copper plating in the centre of the through hole. Bubble collapse in the sonicated Electroless solution would be expected to cause localised heating of the electrolyte, improve mass transport of the Cu-EDTA complex into the through holes and reduce the thickness of the diffusion layer as has been previously proposed by Matsushima et al [14]. Therefore, under ultrasonic conditions, initiation of the electroless reaction would be expected to be faster whereas when conventional agitation was employed the electroless deposition reaction does not appear to have initiated at all in some areas of the through hole leading to voids and poor coverage. In addition, once the reaction has begun, the finer grain structure produced by the effects of ultrasound might be expected to be more catalytic for the electroless plating reaction to continue upon. A recent paper by Byeon and Kim [15] showed that an Electroless Copper deposited under ultrasonic agitation had a finer grain structure and was more catalytic in a methanol steam reforming reaction. A final reason could be the ability of ultrasound to degas a solution. A by-product of electroless copper plating is hydrogen gas which can become entrapped in a PCB through hole and prevent solution flow in the hole or simply block off the area under the bubble preventing plating. As other workers have commented [16], ultrasound would be more likely to prevent this scenario occurring.

It is also interesting to note that there is no effect of ‘delay’ time on the backlight grades. This can be explained by the fact that the catalyst is deposited in the ‘through holes’ of the PCB and is not

on the surface of the board. For this reason it will be much more difficult for the ultrasonically induced microjetting to remove the catalyst.

4. CONCLUSIONS

In this study, where a low concentration catalyst has been used in the metallization of a non-conductive substrate, it has been confirmed that it is necessary to introduce a delay time before ultrasound is switched on if increased plating rates on the surface of the substrate are to be relaised. However when plating the through holes of a PCB, ultrasound can bring about a significant improvement in coverage at low catalyst concentrations and at reduced Electroless Copper plating temperatures. Indeed, the electroless copper coverage at 25 ºC using 40 kHz ultrasound was equivalent to 50 ºC using conventional agitation. Not only does this indicate the potential for using ultrasound to make significant energy savings in electroless copper plating, but it also suggests that it will enable reduced catalyst concentrations to be employed decreasing the amount of a critical (and expensive) raw material (Pd) which in turn will lead to lower manufacturing costs. In addition, the improved coverage observed when electroless copper plating is carried out in an ultrasonic field is very important for the electronics industry generally where miniaturisation is becoming critical with the requirement to plate ever smaller features.

The improvement in electroless copper coverage is thought to stem to a large extent from the finer grain structure of the electroless copper deposit obtained under ultrasound. However other factors such as improved solution flow, reduction of the diffusion layer thickness, localised heating and degassing are also likely to be important.

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