View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by CURVE/open

Low-frequency ‘delay time’ ultrasound and its effect on electroless Cu metallisation of a Pd activated dielectric material

Cobley, A. , Tudela-Montes, I. , Abbas, B. and Mkhlef, B.

Author post-print (accepted) deposited by Coventry University’s Repository

Original citation & hyperlink:
Cobley, A. , Tudela-Montes, I. , Abbas, B. and Mkhlef, B. (2015) Low-frequency ‘delay time’ ultrasound and its effect on electroless Cu metallisation of a Pd activated dielectric material. *Thin Solid Films*, volume 597 : 226-230
http://dx.doi.org/10.1016/j.tsf.2015.11.068

DOI 10.1016/j.tsf.2015.11.068
ISSN 0040-6090

Publisher: Elsevier

NOTICE: this is the author’s version of a work that was accepted for publication in Thin Solid Films. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Thin Solid Films, [597, (2015)]
DOI: 10.1016/j.tsf.2015.11.068

© 2015, Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International
http://creativecommons.org/licenses/by-nc-nd/4.0/

Copyright © and Moral Rights are retained by the author(s) and/ or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.

This document is the author’s post-print version, incorporating any revisions agreed during the peer-review process. Some differences between the published version and this version may remain and you are advised to consult the published version if you wish to cite from it.

Low-frequency ‘delay time’ ultrasound and its effect on electroless Cu metallisation of a Pd activated dielectric material

Andrew J. Cobley, Ignacio Tudela, Bahaa Abbas, Bilal Mkhlef

The Functional Materials Research Group,
Manufacturing and Materials Engineering Faculty Research Centre,
Faculty of Engineering and Computing,
Coventry University,
Priory Street, Coventry, CV1 5FB, UK.

Corresponding author: Andrew J. Cobley, Tel: +44 7706955901, Email: a.cobley@coventry.ac.uk

ABSTRACT: The effect that the presence of low-frequency ultrasound has on the deposition rate of an electroless Cu plating process for the metallisation of a Pd activated dielectric material has been preliminarily studied. Continuous ultrasound during electroless Cu plating had little effect on the deposition rate compared with the standard process under mechanical agitation due to the detrimental effect of cavitation on removing Pd from the dielectric materials. However, the introduction of a ‘delay time’ prior to the introduction of ultrasound resulted in an increase of the deposition rate of up to 26% (7-minute delay time) and suggested that low frequency ultrasound could enable a reduction in electroless copper operating temperatures without a significant decrease in plating rate. Cu coatings produced in such conditions exhibited a significantly enhanced surface coverage with reduced porosity without any undesired effect on the crystal structure.

KEYWORDS: Ultrasound; Sonochemistry; Electroless; Copper; Deposition rate; Porosity; Palladium; PCB

1. Introduction

Electroless Cu plating is widely used in the electronics industry, enabling the metallisation of non-conductive materials and allowing the plating of ‘through holes’ and ‘vias’ in printed circuit boards (PCBs). Nevertheless, the continuous drive to miniaturisation, reduced manufacturing times and more sustainable plating processes means that traditional electroless Cu processes are reaching their limit of capability. In this respect reduced plating temperatures would be desirable not only from an energy and cost saving perspective but would also help to reduce noxious, formaldehyde containing fumes, emanating from the plating solution.

Setting an ultrasonic field in a liquid results in the formation, growth and collapse of bubbles [1] also known as ‘acoustic cavitation’ [2], which bring beneficial effects such as acoustic streaming and micro-jetting, formation of shock waves, mass transport enhancement and surface cleaning to electrochemical applications in general [3] and electroless processes in particular [4]. Different studies have shown a variety of benefits of the use of ultrasound in electroless Cu processes such as enhanced mass transport [5,6], localised heating [5], thinning of the diffusion layer [6] and de-gassing [6-8], resulting in an improved plating of ‘vias’ [6,7] in PCBs and a better surface finish and adhesion to the substrate [8]. The enhancement of the deposition rate in such processes by ultrasound has also been reported in the past for different ultrasonic frequencies (28.2 [5], 40 [9], 300 [10], 500 [10], 530 [11], 800 [10] and 1024 kHz [5]). However, with the notable exception of the work performed by Touyeras et al.[10-12], many of these studies have ignored the importance of the impact that acoustic cavitation might have on the surface concentration

of Pd which is critical to the initiation of electroless Cu deposition on a non-metallic substrate.

When electroless Cu plating a dielectric material a Pd activation stage is first performed as part of the pre-treatment process and this results in the deposition of Pd nanoparticles on the surface of the substrate [13]. If these Pd nanoparticles are not present on the surface of the dielectric or non-conductive substrate then metallisation simply will not occur. Even when they are present, the concentration of Pd and its distribution over the surface to be plated will have a major impact on subsequent plating rates and coverage [14]. Originally the activation of a non-metallic substrate was carried out using a 2 or 3 step process [13][15-18]. The 'activation' stage (1 or 2 steps) would result in a Pd core surrounded by a Sn 'shell'. A further 'acceleration' stage would then largely remove this Sn 'shell' leaving Pd on the surface of the material to be plated which then initiated the electroless Cu reaction. However, in commercial electroless Cu processes such activation procedures have been largely replaced with a single Pd-Sn colloidal system and the 'accelerator' stage is also eliminated by the use of 'self-accelerating' electroless Cu solutions. The majority of studies reported in the literature do not use 'self-accelerating' electroless Cu processes, even though said processes are the most employed in industry and therefore the relevance of these studies to real manufacturing environments has to be questioned.

In this study the influence of low-frequency ultrasound on a Pd-activated 'self-accelerating' electroless Cu process is investigated. The effect of using a 'self-accelerating' electroless Cu on the Pd and Sn concentration of an 'activated' dielectric material is determined whilst, in addition, the importance of understanding how low frequency

ultrasound affects the Pd concentration on the surface of a dielectric material is revealed. Based on this understanding, optimisation of how ultrasound is introduced to the electroless Cu process is reported and in what way it might enable reduced temperature electroless Cu plating. Related to this, the present work introduces an original concept in ultrasound-assisted electroless Cu plating, 'delay time', which may enhance the deposition rate at lower temperatures while not increasing Pd removal from the surface of the 'activated' substrate to be metallised. Finally, the effect of the optimised low-frequency ultrasound on the morphology and crystal structure of the electroless-plated Cu deposit is described.

2. Experimental details

2.1. 'Self-accelerating' electroless Cu plating process

A commercially available 'self-accelerating' electroless Cu plating process supplied by Chestech Ltd was employed in this study (Table 1). The electroless Cu solution is Ethylenediaminetetraacetic acid (EDTA) based and uses formaldehyde as the reducing agent. The solution also contains a number of additives but as this is a commercial product the exact formulation cannot be revealed. A Pd/Sn colloid is deposited on the surface during immersion in the 'Catalyst' solution which contains around 600 ppm of Pd.

2.2. Experimental set-up

All the experiments conducted in 'silent conditions' (i.e. absence of ultrasound) were carried out in a 1000 mL beaker containing 800 mL of the Cu 3350-1 solution continuously stirred with a magnetic stirrer, whereas a 40 kHz 375 TT ultrasonic bath (Langford Electronics UK Ltd) containing 1000 mL of the Cu 3350-1 solution was used in the experiments with ultrasound. The bath was previously characterized by calorimetry

1 [19], showing an ultrasonic power of 0.103 W/cm^3. All the experiments were conducted on
2 test coupons (2.5 x 2.5 cm) prepared from Isola Duraver 104 sheets, a typical PCB laminate
3 material.

4 **2.3. Experimental procedures**

5 *2.3.1. Effect of low-frequency ultrasound on 'self-accelerating' electroless Cu plating*

6 For the evaluation of the influence of ultrasound on the plating rate of the 'self-
7 accelerating' electroless Cu process test coupons underwent the whole regime described in
8 Table 1, where the test coupons were immersed in the Circuposit 3350-1 solution for 25
9 minutes at different temperatures under three different stirring conditions:

10 1. Agitation using a magnetic stirrer (referred to as 'silent' conditions).
11 2. Continuous ultrasound.
12 3. 'Delay time' ultrasound, where the ultrasonic bath was only turned on after a
13 variable 'delay' time as shown in Table 2 below. During the ultrasound 'off' time
14 the electroless Cu solution was agitated using a magnetic stirrer.

15 Deposition rates were determined by the 'weight gain' method whereby test
16 coupons were first dried in an oven at 120 ºC for 24 hours and weighed. They were then
17 coated with Cu using the process detailed in Table 1, and then dried at 120 ºC for 24 hours
18 and weighed again. The plating rate could then be calculated from the weight gain using the
19 following equation:

$$t = \frac{\Delta m}{A\rho} \qquad (1)$$

20

1 where t is the thickness of deposit, Δm is the weight gain due to electroless deposition, A is
2 the area of plated coupon and ρ is the density of plated metal (Cu).

3 Cu coatings plated in electroless Cu electrolytes at 40 ºC in the absence of ultrasound and
4 using 7-minute 'delay' ultrasound were analysed in a Focused Ion Beam - Scanning
5 Electron Microscope (FIB-SEM) (FEI Nova 600 Nanolab Dualbeam system) to evaluate
6 any effect of the optimal ultrasonic agitation conditions on the surface morphology and
7 microstructure of the coatings. Electroless Cu deposits obtained using these same
8 conditions were also analysed by X-Ray Diffraction (XRD) to determine the crystal
9 structure of the Cu coatings. Diffractograms were recorded with a step size of 0.01º for 2θ
10 ranging from 5 to 100º and measuring time of 3.6 seconds per step with an X-Ray
11 diffractometer operating with Cu-Kα radiation.

12 *2.3.2. Effect of low-frequency ultrasound on Pd concentration over the surface of an*
13 *activated substrate*

14 For the investigation into the effects of low-frequency sonication on the Pd-Sn
15 activated dielectric material the test coupons underwent the whole process described in
16 Table 1 except for the Circuposit Electroless Copper 3350-1, where a 'simulated' 3350-1
17 bath under silent conditions and ultrasound was used instead. The 'simulated' electroless
18 Cu solution contained all the elements of the electroless Cu solution except the Cu-
19 containing component to ensure that coupons were not coated with Cu as this would
20 prevent analysis of the Pd content on the surface of the substrate. X-Ray Photoelectron
21 Spectroscopy (XPS) analysis was used to determine the amount of Pd and Sn on the surface
22 of the test coupons after being immersed in the 'simulated' 3350-1 bath for 10 minutes

1 with/without the presence of ultrasound. XPS analysis was conducted in a Thermofisher
2 ESCALAB 250 electron spectrometer equipped with a hemispherical sector energy
3 analyzer.

4 **3. Results and Discussion**

5 Figure 1 displays deposition rates measured on Cu electroless plating experiments
6 conducted at different temperatures under different conditions. It is clear from these results
7 that the main effect on electroless Cu deposition rates is the electrolyte temperature. When
8 comparing experiments carried out under continuous ultrasound (dashed line) with those
9 conducted under silent conditions (continuous line), it is easily observed that the only
10 significant enhancement by ultrasound in terms of deposition rate is achieved at the highest
11 plating temperature (46 ºC). The increase in the deposition rate is in this sense comparable
12 to previous data reported by Tian and Guo [9] under similar ultrasound conditions (16%
13 increase in the present paper vs 20% increase in theirs using a 40 kHz ultrasonic system).

14 These results cannot be interpreted without an understanding of the influence of low-
15 frequency ultrasound on the concentration of Pd on the dielectric material. One of the most
16 common applications of low-frequency ultrasound is in the cleaning of materials [2]. The
17 formation and collapse of cavitation bubbles creates micro-jets which can hit the surface of
18 materials at very high speed [3]. This has a scrubbing effect on the surface of materials
19 removing contaminants and debris leading to very efficient surface cleaning. It was
20 postulated that a very similar effect might be occurring in this case, as the ultrasonically
21 induced micro-jetting could 'scrub' the Pd particles from the surface of the dielectric during
22 the initial immersion in the electroless Cu solution. The reduced Pd concentration on the

surface of the dielectric would then lead to slower initiation of the electroless Cu plating reaction and therefore to lower plating rates. This phenomenon would be most problematic when the plating solution temperature was low and initiation times relatively long. This concept appears to agree with the plating rate results shown in Figure 1 which indicate that at 40 ºC and below, the presence of continuous ultrasound had either no effect or somewhat reduced the plating rates compared to 'silent' conditions. The recommended operating temperature for this particular electroless Cu process is 46 ºC and it can be seen that at this temperature continuous ultrasound has a positive effect on plating rates. At this higher temperature the electroless Cu plating reaction initiation time will be short and therefore the concentration of Pd on the surface of the dielectric will not be so critical. Therefore, the beneficial effects of sonication to an electrochemical process (improved mass transfer, reduced diffusion layer thickness etc.) will far outweigh the negative effect of micro-jetting i.e. some loss of Pd from the substrate surface.

To confirm this theory, different samples of the Pd-activated dielectric material were immersed in the 'simulated' electroless Cu solution under either ultrasound or silent conditions for 4 and 10 minutes, and the surface of the sample was then analysed by XPS to estimate the surface composition in terms of Pd and Sn. The results are shown in Figure 2. After 4-minute immersion in the 'simulated' electroless Cu solution, Pd content in the surface of the samples remained relatively similar whether ultrasound or conventional agitation was employed. Moreover, in both cases Pd content appeared to slightly increase compared to the Pd content of samples that were not immersed in the 'simulated' electroless Cu solution. This would be caused by the depletion of Sn in the surface of the samples after being immersed during 4 minutes in the solution, as Sn content is

significantly reduced in all cases, clearly indicating that the electroless Cu solution is indeed ‘self-accelerating’. In this sense, a Sn ‘shell’ would mask some of the Pd ‘core’ after the ‘Catalyst’ stage. However, when the dwell time was increased to 10 minutes, XPS analysis confirmed that ultrasound could remove virtually all the Pd nanoparticles from the substrate surface (it would not be a Pd-activated dielectric material anymore). This implies that ‘continuous’ sonication at 40 kHz clearly has an undesired effect on the deposition rate for a catalysed electroless Cu process if the Pd nanoparticles on the surface are not ‘protected’ from the action of cavitation phenomena occurring near the surface.

To avoid ultrasonic scrubbing of the Pd from the surface of the dielectric, a ‘delay time’ was introduced before the ultrasonic bath was turned on in the electroless Cu plating stage. The effect of utilising different delay times using an electroless Cu plating temperature of 40 ºC, is shown in Figure 3. It can be seen that, as the delay time was increased up to 7 minutes, the plating rate also rose, further confirming the concept that the removal of Pd from the surface of the Pd-activated dielectric material when continuous ultrasound is applied has a negative impact on plating rates at low plating temperatures. A further increase in the ‘delay time’ (10 minutes) did not show any further improvement in the deposition rate compared to the 7 minute ‘delay time’ although it should be noted that the deposition rate with the 10 minute ‘delay time’ is still significantly higher than under silent conditions. Considering the fact that mechanical agitation (silent conditions) results in a lower plating rate then it is not surprising that if mechanical agitation is employed for 10 minutes (i.e. 40% the total plating time of 25 minutes) then the beneficial effects of sonication do not have sufficient time to realise a further increase in plating rate.

One might initially conceive that the introduction of a 'delay time' contradicts the work of Touyeras et al. [10,11], who suggested that the presence of ultrasound during the electroless Cu plating stage mainly affected the initiation stages of the electroless Cu deposition by removing any remaining Sn from the colloidal catalyst and enhancing the reduction of Pd^{+} to the more catalytic Pd. Nevertheless, high frequency ultrasonic systems were employed in all their studies, whereas a low frequency bath was used in the present work. Mechanical effects are predominant at low frequency ultrasonic fields, whereas chemical effects are predominant at high frequency ultrasonic fields [20]. Therefore, a low frequency ultrasonic field has a negative effect in the early stages of the Cu deposition due to the removal of the Pd catalyst from the substrate, but can generate beneficial thermal effects and enhanced mass transport once the electroless Cu plating reaction has been initiated. Conversely, a high frequency ultrasonic field may have a positive effect in the early stages of the Cu deposition due to the enhancement of the reduction of Pd^{2+} to the more catalytic Pd, whereas no effect would be further observed once the Pd catalyst is covered with the Cu coating. In fact, Touyeras et al. [10,11] reported that, when using higher ultrasonic powers in their high-frequency systems, the Pd catalyst was scrubbed from the surface of the epoxy substrates they used, which agrees with the results reported in this study.

Figure 1 also displays the effect of the introduction of the 7-minute 'delay time' (dotted line) over the range of plating temperatures previously used in the experiments conducted under continuous ultrasound and 'silent' conditions. Although at 25 ºC the introduction of a 7-minute delay in sonication did not have any effect, at 30 ºC the introduction of the delay caused a 60% and 46% increase in plating rates compared to the experiments conducted under continuous ultrasound and 'silent' conditions. Above 30 ºC, the efficacy of the 'delay

time' to increase plating rates progressively decreased as the electroless Cu solution temperature was increased, although it should be noted that at 40 ºC the increase in deposition rate of 20% respectively is not insignificant at all. Indeed PCB manufacturers generally aim for a minimum electroless Cu thickness of approximately 2 µm and the results from this work indicate that this can now be achieved at a reduced plating temperature of 40 ºC in a reasonable plating time. This is an important finding as it suggests that, with careful optimisation of how low-frequency ultrasound is introduced to a Pd-activated electroless Cu process, a significant enhancement in plating rates can be achieved at reduced electrolyte temperature, potentially lowering energy costs and increasing production capacity.

FIB-SEM analysis FIB was performed on Cu coatings produced under 7-minute 'delay time' ultrasound and 'silent' conditions to analyse the effect of the introduction of the 'delay time' ultrasound on the surface morphology and the coating crystal structure. As shown in Figures 4 A and B, the introduction of 7-minute 'delay time' ultrasound during the electroless Cu plating stage showed benefits in terms of improved surface coverage and a significantly lower porosity compared to 'silent' conditions. This was confirmed after analysing the cross-section of the coatings, as a higher number of pores of a larger size were observed in the Cu deposits produced under silent conditions (Figure 4 C) than in those prepared using the more optimised ultrasonic process (Figure 4 D). However, no significant effect of ultrasound was observed on the grain structure of the coatings, as Cu deposits produced under either mechanical agitation (Figure 4 E) or 7-minute delay ultrasound (Figure 4 F) presented similar grain structure and size. No major differences were observed in terms of crystal orientation, as very similar XRD patterns (Figure 5 A)

and virtually identical Relative Texture Coefficients ($RTC_{(hkl)}$) [21] (Figure 5 B) were obtained for the Cu deposits produced under either mechanical agitation or 7-minute delay ultrasound.

4. Conclusions

The results from this study have demonstrated that, if low-frequency ultrasound is to be used to enable low temperature electroless Cu plating rates on a Pd-activated dielectric material, then an understanding of how acoustic cavitation and micro-jetting affect the Pd content on the surface of the substrate is critical. If continuous low-frequency ultrasound is used during 'self-accelerating' electroless Cu plating processes then this will remove Pd from the surface of the material resulting in increased plating initiation times and, subsequently, to lower plating rates particularly at low electrolyte temperatures. The introduction of a 'delay time' before ultrasound is turned on alleviates the issue of Pd removal from the substrate to be plated and enables the beneficial effects of ultrasound on electrochemical processes to be realised. This results in enhanced plating rates at electroless Cu plating temperatures between 30 and 46 ºC. Surface analysis of the electroless Cu coating deposited at 40 ºC using 7-minute 'delay time' ultrasound indicated that an additional benefit of employing sonication during plating is reduced porosity deposition although no effect on the crystal structure orientation was observed.

Acknowledgements

The authors wish to thank the IeMRC and EPSRC for funding the present project. The authors acknowledge the assistance of Dr Geoff West (Loughborough University) for his expertise in carrying out the FIB-SEM analysis and Dr Mike Petty of Loughborough

1 Surface Analysis Ltd for carrying out the XPS measurements. The authors also
2 acknowledge the support of AGAS Electronic Materials Ltd, Graphic Circuits Ltd, Solar
3 Capture Technologies Ltd, The Institute of Materials Finishing and the Institute of Circuit
4 Technology.

5

1 **References**

2 [1] K. Suslick, The chemical effects of ultrasound Scientific American 80 (1989) 260.

3 [2] G.J. Louisnard O, Acoustic cavitationFeng H, Barbosa-Canovas G, Weiss J (Ed.),
4 Ultrasound Technologies for Food and Bioprocessing, Springer, New York-Dordrecht-
5 Heidelberg-London, 2011.

6 [3] J. González-García, M.D. Esclapez, P. Bonete, Y.V. Hernández, L.G. Garretón, V.
7 Sáez, Current topics on sonoelectrochemistry, Ultrasonics 50 (2010) 318-322.

8 [4] A.J. Cobley, T.J. Mason, V. Saez, Review of effect of ultrasound on electroless plating
9 processes, Trans. Inst. Met. Finish. 89 (2011) 303-309.

10 [5] Y. Zhao, C. Bao, R. Feng, Z. Chen, Electroless coating of copper on ceramic in an
11 ultrasonic field, Ultrason. Sonochem. 2 (1995) S99-S103.

12 [6] T. Matsushima, H. Habaki, J. Kawasaki, Electroless Copper Deposition in a Blind Via
13 Hole of Printed Wiring Board. Uniform Copper Deposition by Axial Temperature Gradient,
14 Electrochem 68 (2000) 568-571.

15 [7] S.-. Kou, A. Hung, Plating of small blind vias, IEEE Trans. Electron. Packag. Manuf.
16 22 (1999) 202-208.

17 [8] Y. Lu, Improvement of copper plating adhesion on silane modified PET film by
18 ultrasonic-assisted electroless deposition, Appl. Surf. Sci. 256 (2010) 3554-3558.

19 [9] Q.-. Tian, X.-. Guo, Electroless copper plating on microcellular polyurethane foam,
20 Trans Nonferrous Met Soc China 20 (2010) s283-s287.

21 [10] F. Touyeras, J.Y. Hihn, X. Bourgoin, B. Jacques, L. Hallez, V. Branger, Effects of
22 ultrasonic irradiation on the properties of coatings obtained by electroless plating and
23 electro plating, Ultrason. Sonochem. 12 (2005) 13-19.

24 [11] F. Touyeras, J.-. Hihn, M.-. Doche, X. Roizard, Electroless copper coating of epoxide
25 plates in an ultrasonic field, Ultrason. Sonochem. 8 (2001) 285-290.

26 [12] F. Touyeras, J.Y. Hihn, S. Delalande, R. Viennet, M.L. Doche, Ultrasound influence
27 on the activation step before electroless coating, Ultrason. Sonochem. 10 (2003) 363-368.

28 [13] T. Osaka, H. Takematsu, K. Nihei, Study on activation and acceleration by mixed
29 $PdCl_2/SnCl_2$ catalysts for electroless metal deposition, J. Electrochem. Soc. 127 (1980)
30 1021-1029.

[14] D.J. Auerbach, C.R. Brundle, D.C. Miller, Surface Analysis and Characterization of Large Printed-Circuit-Board Circuitization Process Steps, IBM J Res Dev 32 (1988) 669-681.

[15] J.J. Grunwald, S. Gottesfeld, D. Laser, Auger spectroscopic study of the catalysis process for electroless copper plating, Plat. Surf. Finish. 68 (1981) 71-74.

[16] B.J. Meenan, N.M.D. Brown, J.W. Wilson, Characterisation of a $PdCl_2$/$SnCl_2$ electroless plating catalyst system adsorbed on barium titanate-based electroactive ceramics, Appl. Surf. Sci. 74 (1994) 221-233.

[17] T. Osaka, H. Nagasaka, F. Goto, Electron diffraction study on mixed $PdCl_2$/$SnCl_2$ catalysts for electroless plating, J. Electrochem. Soc. 127 (1980) 2343-2346.

[18] M.C. Burrell, G.A. Smith, J.J. Chera, Characterization of $PdCl_2$/$SnCl_2$ metallization catalysts on a polyetherimide surface by XPS and RBS, Surf. Interface Anal. 11 (1988) 160-164.

[19] C. Ratoarinoro, A. Wilhelm, J. Berlan, H. Delmas, Power measurement in sonochemistry, Ultrason. Sonochem. 2 (1995) S43-5.

[20] A.J. Cobley, T.J. Mason, V. Saez, Review of effect of ultrasound on electroless plating processes, Trans. Inst. Met. Finish. 89 (2011) 303-309.

[21] L.P. Berube, G. L'Esperance, Quantitative method of determining the degree of texture of zinc electrodeposits, J. Electrochem. Soc. 136 (1989) 2314-2315.

Table and Figure Captions

Table 1. Commercial 'self-accelerating' electroless Cu plating process (Chestech Ltd) used in this study.

Table 2. 'Delay' times used before introduction of 40 kHz ultrasound to electroless copper solution at 40 ºC

Figure 1. Deposition rate of 'self-accelerating' electroless Cu plating process under silent conditions (solid line), continuous 40 kHz ultrasound (dashed line) and 7-minute 'delay time' 40 kHz ultrasound' (dotted line) at various temperatures.

Figure 2. Evolution of Pd content (●) and Sn content (○) vs time on the surface of epoxy test coupons immersed in a 'simulated' electroless Cu solution under silent conditions (dashed lines) and continuous 40 kHz ultrasound (solid lines).

Figure 3. Deposition rate of 'self-accelerating' electroless Cu plating process under ultrasound after introducing different 'delay times' before sonication.

Figure 4. FIB-SEM images of Cu deposits plated under silent conditions (left) and under 7-minute delay ultrasound (right): surface morphology (A and B), cross-section (C and D) and ion-beam high contrast cross-section (E and F).

Figure 5. (A) XRD spectra for Cu coatings electroless deposited under 'silent' conditions and 7-minute 'delay time' ultrasound (7-min delay). (B) $RTC_{(hkl)}$ coefficients estimated for the different crystal planes observed in Cu coatings electroless deposited under silent conditions (black) and 7-minute 'delay time' ultrasound (white).

Process step	Bath composition	Temperature (°C)	Time (minutes)
Conditioner 3323	5% (v/v) Conditioner 3323	50	5
Catalyst Pre-dip 3340	270 g/l Pre-dip 3340	40	1
Catalyst 3344	270 g/l Pre-dip 3340 3% (v/v) Catalyst 3344	40	5
Electroless copper 3350-1	3.2 g/l $CuCl_2$ 7.8 g/l NaOH 3 g/l CH_2O 35 g/l EDTA	40	25

Table One

Agitation by magnetic stirrer - 'Delay' time (minutes)	Agitation by 40 kHz Ultrasound (minutes)
25	0
2	23
4	21
7	18
10	15

Table Two

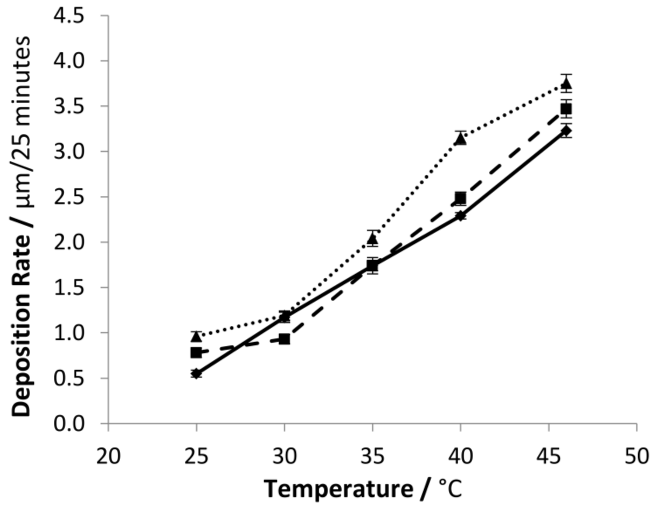


Figure One

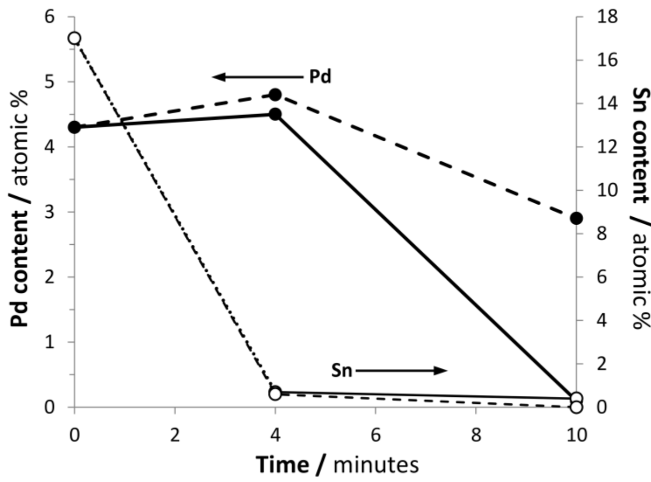


Figure Two

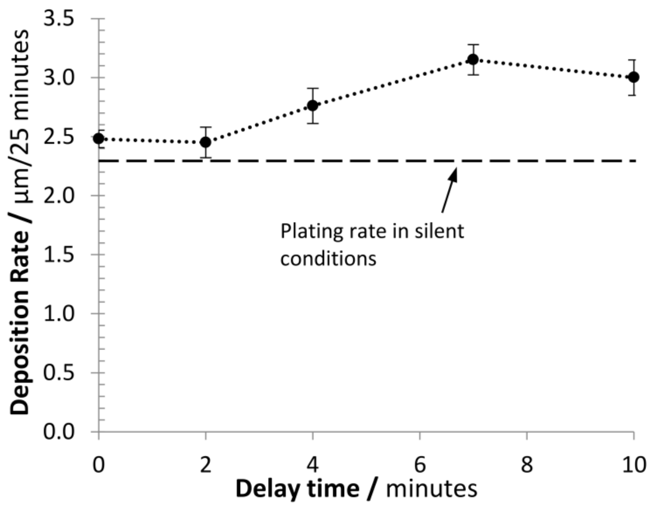
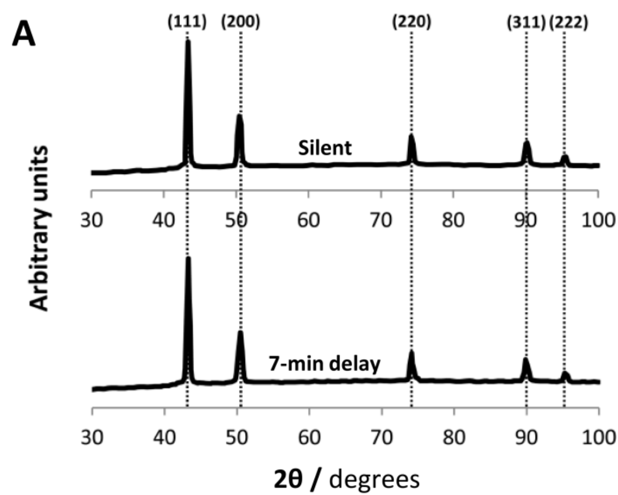


Figure Three

Figure Four unavailable



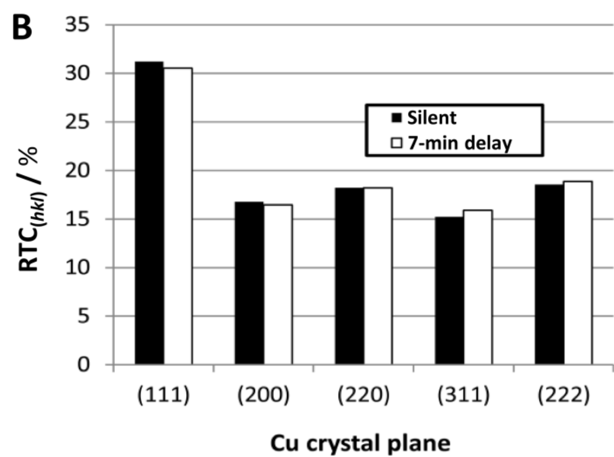


Figure Five