Coventry University

MASTER OF SCIENCE BY RESEARCH

# Examination of the effect of ultrasound on electroless copper plating

Abbas, Bahaa

*Award date:*
2013

*Awarding institution:*
Coventry University

Link to publication

# Examination of the effect of ultrasound on electroless copper plating

Bahaa Abbas

A thesis submitted in partial fulfilment of the University's requirements
for the Masters by Research program

September 2012

Sonochemistry Centre
Faculty of Health and Life Sciences, Coventry University

# Abstract

The main aims of this project were to:-

- Use ultrasound to enhance the plating rate of an electroless copper process at low temperatures
- Replace formaldehyde by using another reducing agent, which is more environmentally beneficial to the industry.

The effects of ultrasound on the electroless copper plating of epoxy substrates using different frequencies (40 and 850 kHz) has been investigated at different temperatures (25, 30, 35, 40, 45 and 50ºC) with different reducing agents (formaldehyde and glyoxylic acid) and in the presence and absence of air bubbling. The conventional plating rate in this process is (1.25*µm /25 minutes*) at 46ºC. Ultrasound was applied during the plating process and also with an added delay at the start of the plating process. Several parameters were monitored such as plating rate (via calculation of weight gain), stability of the plating bath (UV) the reflectance percentage (Gloss Meter), test of substrate surface by scanning electronic microscope (SEM) and X-ray Photoelectron Spectroscopy (XPS). The adhesion of the copper layer on the substrate surface also was examined. The results obtained clearly indicate that use of 40 kHz sonication leads to the highest plating rate at 35 and 40ºC when a time delay of 7 minutes is introduced before applying ultrasound. The deposition rate increased from 1.43*µm/25 minutes* to 1.65*µm/25 minutes* at 35$^{o}$C and from 1.86*µm/25 minutes* to 2.54 *µm/25 minutes* at 40$^{o}$C**.** Sonication was also found to be unhelpful at 25 and 30 ºC where the deposition rate was found to decrease at these temperatures at both frequencies (40 and 850 kHz) from 0.75 *µm*/25 *minutes* to 0.27*µm*/25 *minutes* at 25$^{o}$C and from 1.18*µm/25 minutes* to 1.11*µm/25 minutes* at 30$^{o}$C. Introduction of air bubbling reduced the plating rate but enhanced the copper bath stability at 40ºC. All results showed that the plating rate was much higher with formaldehyde than with glyoxylic acid. SEM results also show that application of ultrasound causes a fine grain structure which impacts on the colour of the substrate surface, as the gloss meter results show.

Unfortunately UV results indicate that with sonication it appears that the stability of the electroless plating bath is much reduced with copper precipitating out of the solution after sonication. This indicates that the use of this technology may prove problematical in 'real life' conditions.

# ACKNOWLEDGEMENT

I would like to thank Dr. L. Paniwnyk, Dr. A. Cobely and Dr. Johan Graves for their guidance, advice and encouragement throughout the duration of study. Thanks to staff and students in the sonochemistry centre group for their supports. Thanks to the staff at Coventry University for their support.

Last I would like to thank my family, friends especially Mr Bilal mekhlef for their support and encouragement throughout the past two years.

# List of Contents

**Chapter Three : Results and discussion**

**Chapter Four : Conclusion and Further work**

# 1.0 Introduction

## 1.1 Aims and Objectives

The main aim of this project was to investigate the ability of ultrasound to increase the plating rate of an electroless copper plating process at low temperature. Electroless copper processing is used widely within most electronic manufacturing, which employs it to produce electronic devices such as TVs, laptops and mobile phones. By reducing the energy consumption of the electoless plating process the overall production costs of these types of products can be reduced as well. Since there is a high ratio of people currently using these electronic devices, this means consumers would also benefit. Electroless copper plating is also used widely within the manufacture of photovoltaic cells which is considered as being a new ‘green’ technology to convert the energy of light into electrical energy.

## 1.2 The use of electroless plating in Printed Circuit Board manufacture

Currently, all electronic equipment such as TVs, laptops and phones use different types of polymers in their manufacture and these polymers are generally non-conductive materials. These polymers are used because they have low production costs, are light weight and also have a good resistance to high temperatures. Polymers are often used in the manufacturing of printed circuit boards (PCBs) (Figure.1) as a base substrate onto which different electronic circuits are then placed. These polymers, or substrates, need to be selectively conductive and hence they must be coated by a conductive metallic layer such as copper or nickel. This conductive layer will then enable the interconnection between different electronic components which are placed on the surface of the substrate (Coombs 1988). Epoxy resin material is one of the polymer substrates which has wide usage within the printed circuit boards (PCBs) and multi layer board (MLBs) industries (Goosey and Poole 2004). The electroless copper plating process can be considered to be a metallization process that enables the properties of the polymer, such as light weight and low cost, to be combined with those of the properties of copper metal, such as good conductivity and ductility (Mkhlef 2010).

Figure 1- Printed circuit boards (PCBs) (printed circuit board n.d.)

Electroless copper plating is normally employed to generate conductive layers on the surface of polymers that are used within the manufacture of printed circuit boards (PCBs). However with the further development of electronic products such as laptops and new smart phones, a further demand to use smaller printed circuit boards has emerged. Therefore, new substrate boards have been produced and utilized within the electronic manufacturing industry, such as multi layer boards (MLBs) and double-sided circuit boards ((Hanna, Hamid and Aal 2004). In these boards the electroless copper plating allows an electronic interconnection between the different components placed on each of the surfaces of the board. Holes are produced on the circuit boards by drilling both sides of the board using a drilling machine (Coombs 1988) (Fig 2). The prime aim of these holes is to allow conductivity from one layer of the board to another layer on a double circuit board or to build up the interface among different layers in the MLBs (Coombs 1988).

Figure 2, Holes inside PCB between different layers (H.T.F.C 2007)

Now with further demands from European manufacturers to adopt more green and environmentally friendly processes, in order to replace the traditional electroplating process, attention has been focused towards finding alternative methods that could avoid the usage of high temperatures, and large water consumption, that are currently being employed by these industries (Cobley 2007).

The traditional electroless copper plating method involves using a few steps. Firstly, a conditioning agent is used to clean and remove all the organic materials and impurities from the surface of the polymer/substrate that is about to be plated. This is followed with water rinsing of the substrates.

Secondly, the catalysation step is then applied. The catalyst contains a palladium-tin colloid, which is a substance that is microscopically dispersed evenly throughout another substance, and leaves the surface of the substrate material covered with palladium metal. When the palladium covers the surface, it will activate this surface in order to react with the subsequent copper plating. When palladium is not present at the surface of the substrate, the subsequent copper plating will not stick to the surface of the material that is being plated (Touyeras *et al.* 2005).

The electroless copper plating mixture is eventually applied. This contains a reducing agent which is normally formaldehyde and an oxidation reaction then occurs that produces copper deposition on the polymeric substrate material. The initial copper deposit can be thin (Hwangbo and Song 2011) which will then require further electroplating to increase the thickness of the final deposit if necessary. However printed circuit board manufacturers still prefer utilizing the traditional electroless copper plating processes due to their low economic cost compared to other methods.

Although electroless copper plating has been used for many years, there are some difficulties which are involved in this plating method. As a result electronic manufacturers are trying to look for alternative reagents and/or procedures. Amongst these difficulties are:

- High temperatures involved in the electroless plating baths.

- A generally unstable process requiring the addition of chemicals to avoid copper precipitation.
- Carcinogenic nature of some of the chemicals involved eg. formaldehyde
- Environmentally unwanted complexing agents, such as EDTA.
- High water consumption due to the large number of process steps and rinse tanks.

As a result these issues must be overcome to bring the process of electroless copper plating into a more environmentally friendly age.

### 1.2.1 Electrochemical methods of metal deposition

#### A. Electroplating

Electroplating processes are used in the manufacture of PCBs, in photovoltaic production and also in the surface finishing industry, for example in jewellery and coin plating (Katsuma 1995). It is mainly used for depositing a layer of material to bestow a desired property (e.g., abrasion and wear resistance, corrosion protection, decorative qualities, etc.) to a surface that otherwise lacks that property. Electroplating is a plating process in which metal ions in a solution are moved by an electric field to coat an electrode. The process uses an electrical current to reduce the cation of a required material, such as a metal, from a solution and subsequently uses them to coat a conductive object with a thin layer of that material. The electroplating method is well known for its ability to deposit a single metal layer on the substrate surface and is known as electrodeposition. The substrate to be plated is the cathode of the circuit and the anode normally consists of the metal which is required to be plated onto the cathode. The cathode and anode are immersed in a solution called the electrolyte, which contains more than one dissolved metal salt as well as other ions that will allow electrical current to be transferred (Poyner 1988). The cathode and anode in the electroplating cell are connected to an external provider of direct current such as a battery, or more commonly, a rectifier. The cathode is connected to the negative terminal, and the anode is connected to the positive terminal of the supply. When the external power supply is turned on, the metal from the anode is oxidized from the zero valence state to form cations with a positive charge. These cations associate with the anions in the solution. The cations are reduced at the cathode to deposit in the metallic zero valence state. For example, in an acid solution, copper is oxidized at the anode to $Cu^{2+}$ by losing two electrons. The $Cu^{2+}$ associates with the anion $SO_4^{2-}$ in the solution to form copper sulphate. At the cathode, the $Cu^{2+}$ is reduced to metallic copper by gaining two electrons. The result is the effective transfer of copper from the anode source to a plate covering the cathode (Poyner 1988). As shown in Fig (3) electro copper plating.

$Cu \longrightarrow Cu^{2+} + 2e$ ........... Eq 1  Anode
$Cu^{2+} + 2e \longrightarrow Cu$ ........... Eq 2  Cathode

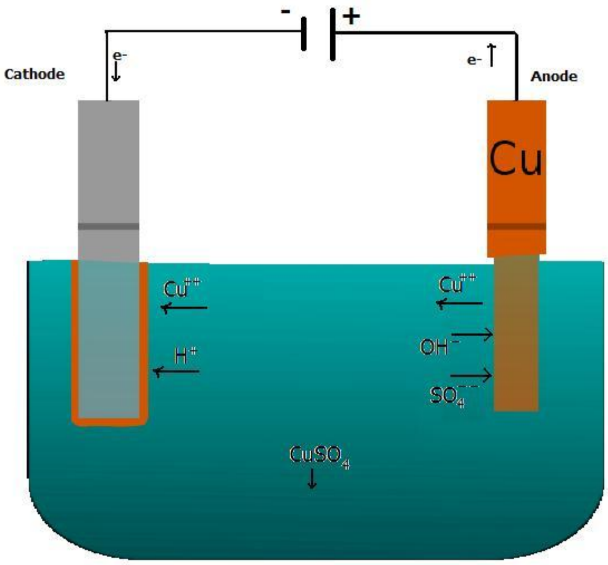


Figure (3) Electro copper plating process

Several electroplating processes might use a non-consumable anode such as iridium dioxide. In this method, an ion of the metal to be plated is present in the bath and must always be replenished in the bath as they are drawn out of the solution and not replaced when they are deposited onto the cathode/substrate.

### B. Electroless copper plating

There is a simple difference between electro plating and electroless plating in that the deposition of metals can be achieved without using an electrical current. It is sometimes referred to as chemical plating as the chemicals in the formulation solution affect the final metallic deposit. The main constituents of the electroless plating solution are an aqueous solution of the chemical containing the metal ions to be deposited and a chemical reducing agent (Gan *et al* 2007). Often a solution containing a catalyst such as palladium chloride is also present, particularly with a nonconductive substrate, in order to activate the substrate surface prior to plating. When the catalyst activated substrate is immersed into the electroless copper plating bath some areas on this substrate turn out to be cathodic and others to be anodic. The electroless copper plating solution contains a reducing agent, such as formaldehyde, which oxidizes the anodic areas and this oxidation releases electrons which are then used in the cathodic areas to reduce the metal ions in the solution to deposit metal onto the substrate. However this technique can result in a number of problems such as a low plating rate, poor adhesion of the metal to the substrate, high operating temperatures that could reach up to 70$^o$C, which also leads to high energy consumption and/or the use of strong reducing agents such as the carcinogenic formaldehyde (HCHO). Formaldehyde is highly toxic to humans and even short term exposure to formaldehyde irritates the eyes, causing pain, redness, blurred vision and severe eye watering (Cheng *et al*. 1997).

Despite these disadvantages the electroless copper process has been successfully used for over 40 years (Cobley 2007). The process consists of three operations 1) conditioning, 2) activation, and finally 3) deposition.

Conditioning

The cleaning process starts with a conditioning solution, normally alkaline, which is used to remove all impurities and organic materials from the substrate surface.

Activation

The activation process consists of two stages.

i) a pre-dip stage, which prevents material being dragged into the catalyst bath from previous stages. It is a preventative step in order to protect the expensive activation (also called catalyst) bath.

ii) an activation stage, which consists of an activation bath containing hydrochloric acid, tin chloride and palladium chloride. The $Sn^{+2}$ ion reduces the $Pd^{+2}$ to Pd, which is deposited on the activated substrate.

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd \quad ................ \text{Eq.3}$$

Figure. 4 “Shows structure of the tin-palladium agglomerate and mechanism of dissolution, particles with negative charges are adsorbed on the substrate surface” (Touyeras *et al*. 2005).

In this case, the activation steps can be conducted in a single step, and the activation step takes place using Pd solution stabilized by a colloidal protective suspension composed of divalent (Sn) and Pd ions and chlorhydric acid. Some tetravalent (Sn) is added to facilitate hydrophobic substrate wet ability (Touyeras *et al*. 2005).

Reactions that occur in the bath and lead to the beginning of copper coating can be illustrated by the following:

$$Pd^{2+} + Sn^{2+} + 4Cl^{-} \rightarrow Sn^{2+}(PdCl_4)^{2-} \text{ ......... Eq.4}$$

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd$$

Deposition

The last process is copper deposition. There are two types of electroless copper baths.
a) heavy deposition baths (designed to produce deposits of 1.9 to 3.1 µm of copper) and
b) light deposition baths (designed to produce deposits of 0.5 to 1.0 µm). Light deposition has to be followed by electrolytic copper plating in order to increase the copper layer density.

Chemicals involved in this process are as follows:-

Formaldehyde is present in light deposition baths in a concentration of 3 to 5 g/L and as high as 10 g/L in heavy deposition baths, EDTA, sodium hydroxide and a copper salt (such as copper chloride or copper sulphate) are also present. In the reaction, catalyzed by palladium, formaldehyde reduces the copper ion to metallic copper.

$$2Cu^{2+} + 2HCHO + 5OH^{-} \rightarrow 2Cu + 2HCO_2^{-} + H_2 + 2H_2O + OH^{\bullet} \quad \ldots\ldots\ldots \text{Eq. 5}$$

In order to maintain the plating baths at optimum performance levels plating chemicals need to be frequently replenished in the plating bath as they are used up during the reaction process.

## 1.3 Ultrasound

Ultrasound is well known for its ability to provide a form of energy for different types of chemical reactions. It travels through a medium, often a liquid, via vibrational motion. This vibrational motion can be visualised as the ripples on water formed when a stone is dropped into it (Mason and Lorimer 2002), as sound itself is considered as moving through a series of compression and rarefaction waves. During the rarefaction cycle, the space between the molecules of a solution is increased, with more of the large negative pressure produced via rarefaction; the average space between the molecules of the solution can go over the critical molecular space which is required to hold the solution intact. When this critical point is reached, the solution molecules break away from each other forming cavities, or microbubbles, within the liquid itself, which can then be filled with vapour previously dissolved in the bulk liquid.

Ultrasound is the name given to the form of sound waves that have a frequency beyond the capacity of normal human hearing. The highest frequency that the human ear is able to respond to is approximately 16 kHz to 18 kHz. This marks the end of the sonic range and the beginning of the ultrasonic range. The use of ultrasound with this higher frequency range can be divided generally into two areas. The first area involves low amplitude (higher frequency) propagation, and is commonly referred to as “low power” or “high frequency ultrasound”. Typically, low amplitude waves are used to measure the velocity and absorption coefficient of the wave in a medium within 2 to 10 MHz range, ultrasound at this range is used in medical scanning. The second area involves high power (low frequency) sonic waves has the frequency range between 20 kHz and 1000 kHz which is used for cleaning, plastic welding and more recently to affect chemical reactivity (Mason 1999).

### 1.3.1 Cavitation

Ultrasound is not able to produce chemical effects directly by an interaction between the ultrasound waves and the substance. As result, some type of indirect interaction is required in order to produce chemical effects and this occurs as the result of the formation, growth and the collapse of the microbubbles or cavities (Mason and Lorimer 2002). There are two kinds of cavitation. Firstly, stable cavitation where microbubbles are created at low intensities, oscillate in the liquid with a lifetime of many cycles and are easily observed with the human eye. The second type of cavitation is known as transient cavitation where microbubbles are only able to exist for a few acoustic cycles. These microbubbles can grow during rarefaction cycles and are able to expand to at least double their initial size. However they eventually reach an unstable size where they either disappear or produce smaller microbubbles that then collapse violently during the subsequent compression wave. The combined effect of ultrasonic cavitation is therefore introduced both via the eventual collapse of the unstable transient cavitation microbubbles in addition to the oscillation of the more stable microbubbles (Mason and Lorimer 2002). It has been confirmed that when this collapse occurs at the frequency of 20 kHz (using an ultrasonic probe), a temperature up to 5000 K (4727$^{o}$C) and a pressure of 2000 atmosphere could be produced.

Figure 5 Development and collapse of cavitation (organic-chemistry.org)

Sonochemistry normally uses the power of ultrasound in the frequency range between 20 and 850 KHz as at these frequencies, enough acoustic energy can be generated to induce cavitation in a liquid. If a cavitation bubble is formed at a substrate surface eventual collapse of that bubble occurs in an asymmetric way resulting in the formation of a high speed micro-jet which is forced towards the substrate surface leading to good physical effects (Mason *et al*. 2011). These micro-jets are able to enhance the plating processes by thinning of the diffusion layer at the substrate surface during the plating process and by enabling a more uniform coverage of the substrate surface with the metal coating itself. Microjets can also break down the particle size and increase the surface area of the substrate (Huang, Xie and Ma 2011). Furthermore, these micro-jets are able to clean the surface to enable more effective adhesion and stronger bonds between the substrate and metal plated onto the surface. The use of ultrasonic irradiation also induces mass transfer enhancement (Mason 1999), and a good mixing of the chemical species and high mass transfer coefficient values arise as a result. Within the liquid, the cavitation microbubbles can be considered as micro-reactors where high local temperatures and pressures can be reached (Mason and Lorimer 2002). Many contaminants, like colloidal palladium, which form during the activation processes, can be removed from the surface that is about to be plated by the influence of ultrasound (Touyeras *et al.* 2001).

### 1.3.2 Sonochemistry equipment

Sonochemistry, or the application of power ultrasound to chemical processes, is an area which has undergone very intensive research and development in the last 15−20 years with respect to both its range of application and the methods employed for its implementation on an industrial manufacturing scale. Ultrasound is employed in many different applications such as in medical applications, in the electronic industry, food industry, and in wastewater treatment. These applications and the equipment used depend on the frequency that is utilized.

#### 1.3.2.1 Ultrasonic bath

This type of ultrasonic device is preferred for applications involving low ultrasonic power using ultrasound frequencies between 40-100 kHz (Mason and Peters 2002). The frequency and power of an ultrasonic bath depends upon the type and number of transducers employed in its design. In the last few years, the appearance of the multi-frequency ultrasonic bath has improved the quality and the influence of the ultrasonic bath performance. This type of ultrasonic bath can be used to apply a wide frequency range between 100 to 850 kHz thus allowing for a wider processing ability.

Figure (6) Ultrasonic bath cleaners (40 kHz) (UltraWave 2012)

Ultrasonic baths are normally inexpensive and the cavitation effect is generally well distributed through the bath liquid (Mason and Lorimer 2002). This device is well known and has a wide usage in many areas, such as wastewater treatment, cleaning processes, the food industry, and pharmaceutical industry (Lynnworth 1974).

Figure (7) Ultrasonic bath (550 850 and 1150 kHz) (Shinka Industry n.d.)

### 1.3.2.2 Ultrasonic probe

This type of ultrasonic device has been introduced particularly to increase the amount of ultrasonic power available to a reaction and can introduce the energy directly into the system, rather than relying on its transfer via a water tank, or the reactor walls, that are used in the ultrasonic bath (Mason and Peters 2002). One of the most important advantages of this system is the availability of this system to be tuned to the most effective frequency to give optimum performances. Figure (8)

Figure (8) Ultrasonic probe 20 kHz (Nano Lab 2009)

### 1.3.3 Ultrasonic Applications

Recently, there has been an expansion of interest in the industrial applications of low-frequency (high-energy) power ultrasound that has a frequency ranging between 20 kHz and 2 MHz (Mason and Lorimer 2002). Power ultrasound is considered to be a technology offering very important advantages in chemical processing such as its ability to increase mass transfer rates, to aid fluid degasification, in cleaning a wide variety of items, its ability to generate free radicals for oxidation purposes and producing microjets for surface activation/cleaning (Carcel *et al*. 2007). These effects are recognized to be caused by the creation and strong collapse of the microbubbles within the liquid system.

#### 1.3.3.1 In the Food Industry

Currently, ultrasound has a wide usage within the food industries in areas such as meat processing (Carcel *et al*. 2007). Carcel *et al*. 2007 had carried out experiments to confirm that the use of ultrasound can be very effective on the meat brining process. In their work, high intensity ultrasound was employed. An ultrasonic probe at 20 kHz was employed and results showed that the influence of ultrasound on the mass transfer process during meat brining depended on the intensity of ultrasound applied, coupled with an increase in the NaCl content of the brining solution. When a bubble collapses close to a solid surface, microjets are produced in the direction of the surface, which can affect the mass transfer by disturbing the boundary layers (Carcel *et al*. 2007). More effective brining was achieved due to greater penetration of the brining solution when applying sonication.

#### 1.3.3.2 In Wastewater Treatment

For wastewater treatment, traditional methods such as using high and low speed blending and chemical treatments have been widely employed on a laboratory-scale to disperse particles associated with micro-organisms (Gibson *et al.* 2009). Ultrasound has been utilized to disrupt these particles and reduce their size. High energy microjets and shock waves produced by the effect of cavitation are confirmed to be the main reasons behind the ability of ultrasound to reduce and disrupt the particles. The fraction of particles reduced in size by ultrasound at 20.3 kHz was affected by the particles origin and concentration and increased with increasing particle size. In contrast, with other methods for wastewater treatment ultrasound did not need the addition and subsequent discharge of any additional chemicals, which is often required with other chemical treatments.

An ultrasonic bath with frequency of 850 kHz has been used for azo dye degradation (Rehorek, Tauber and Gubitz 2004). This frequency at power 60, 90 and 120 W was used for the degradation of industrial azo dyes acid orange 5 and 52 and reactive orange 16 and 107. The results which were obtained showed that ultrasound was able to effectively mineralize azo dyes to non-toxic end products, which was confirmed by employing the respiratory inhibition test of *pseudomonas putida*. All investigated dyes were degraded and decolorized within 3-15 hours with 850 kHz at 90 W and within 1-4 hours with 850 kHz at 120 W. Although the azo dyes are not toxic themselves, they are cleaved via microorganisms to form potentially carcinogenic aromatic amines, which are likely to occur in river sediments. The formation of the aromatic amines can be avoided normally by applying oxidative processes. As ultrasound has the ability to produce $OH^{\bullet}$ free radicals these radicals also have an oxidative nature, which can be used to degrade the azo dyes and to introduce a safe wastewater treatment with non toxic and stable end products (Rehorek, Tauber and Gubitz 2004).

#### 1.3.3.3 In Medical Applications

The use of ultrasound is very well known in medical imaging as it is employed as a tool for pre-natal image scanning and also as a diagnostic procedure (Matsumoto et al. 2005). Ultrasound is generally used in medicine to view the internal organs of the body particularly the developing fetus. The ultrasound used within this area has a frequency range between 2 and 10 MHz.

## 1.4 Ultrasound in Electroplating and in Electroless plating

Zhao *et al*. (1995) and Malik and Ray (2009) have investigated the effect of ultrasound on electroplating and electroless copper plating. In Zhao's work, the influence of the application of ultrasound as well as the influence of sonication time has been determined. They confirmed that applying ultrasound during electroless copper plating increases the production rate of the copper coating. This makes the plating process faster by around 5-10 minutes at very low processing temperatures of 25- 40 $^{o}$C (Zhao *et al*. 1995). Moreover, the adhesion strength between the substrate surface and the copper deposit was found to be increased. Subsequently it was also determined that using ultrasound produced a very rough Acrylonitrile Butadiene Styrene (ABS) surface which could secure good adhesion between the Acrylonitrile Butadiene Styrene (ABS) surface and the electroless copper plating (Zhao *et al*. 1998).

Malik and Ray (2009) investigated the influence of ultrasound on the morphology of the electrodeposited copper. In this work, the effect of temperature and ultrasound on the electro-chemistry principle was examined by adding the impact of sonication to synthesize ultra-fine grains at low temperatures. Malik and Ray (2009) confirmed that ultrasound created an enhanced nucleation process by filling the gap between any two adjacent molecules thus leading to a more compact mass. They have attributed these results to mass transportation caused via the application of ultrasound. Additionally, they have suggested that ultrasound was effective in terms of degassing the electrode surface, which leads to better adhesion between the deposit and the surface and also leads to a brighter deposit.

The effect of ultrasound on electroless and electrolytic nickel plating was examined by Katsuyoshi (2000). For electroless nickel deposition the deposition rate associated with using 45 kHz ultrasound frequency showed a three-fold increase when compared to silent conditions (Kobayashi, Chiba and Minami 2000). In addition, he suggested that the diffusion of $Ni^{2+}$ was accelerated as a result of the imposition of ultrasound due to enhanced mass transfer and mixing. For electrolytic nickel plating, the charge transfer reaction was endorsed, particularly when ultrasound frequencies of 28 kHz and 45 kHz were utilized.

The effect of ultrasound on electrolytic deposition was also investigated by Walker (1997), who confirmed that ultrasound could improve the cathodic current efficiency of zinc electro deposited from a dilute alkaline bath. It also enhanced the copper electro deposited from a dilute acidic sulphate bath. These improvements were attributed to the ability of ultrasound to produce cavitation and degassing, which could reduce the concentration polarization observed during electro deposition and thus considerably increase the cathodic current efficiency (Walker 1997).

The effect of ultrasonic operation on electroless deposition and copper adhesion on silan modified polyethylene terephthalate (PET) was examined by Lu (2010). 40 kHz ultrasonic frequency with 120 W power was used for these experiments. All the results that were achieved in this work confirmed that use of ultrasound causes fast deposition and formation of better membranes for electroless copper deposition. SEM images have shown that the copper film is polycrystalline with small grain structure and grain boundaries which leads to an enhancement of the electrical conductivity of copper from $7.9 \times 10^4$ to $2.1 \times 10^5$ S/cm.

Yongjun Hu *et al.* (2011) had studied the effect of ultrasonic waves on electroless nickel plating at low temperature but used copper as a substrate to be plated at 50 $^oC$. Again 40 kHz sonication was used in this work resulting in an enhanced deposition rate with a finer grained deposit which appeared to be roughly spherical as viewed by SEM.

The effect of low frequency on electroless plating was also investigated by Bulasara in (2012). Here a frequency of 37 kHz sonication resulted in a faster plating rate, higher plating efficiency, greater metal thickness and increased values of effective porosity of the final deposit, that were attributed to the mass transfer enhancement by the effect of ultrasound (Bulasara *et al*. 2012).

The influence of ultrasound on the activation step before electroless plating was examined by Touyeras et al. (2003) and Myeon (2011). In 2003, Touyeras applied sonication, at a constant frequency of 530 kHz, during the activation step and also during the first two minutes of the electroless copper plating. Applying ultrasound during the activation step indicated that the application of the ultrasonic irradiation in electroless plating can influence several properties of the deposit plating rate and practical adhesion. Since most of the observed effects of ultrasound in the chemical process are thought to be due to the cavitation effects together with micro-streaming, the application of ultrasound would influence the behaviour of electroless deposition (Touyeras *et al*. 2005). In 2011, Lee *et al* used 40 kHz sonication on a Pd activation process during electroless silver plating. The influence of ultrasound caused smaller Pd particles that led to a decrease in the induction time during the plating process and resulted in a smoother deposition surface according to SEM and AFM analysis (Lee *et al*. 2011).

Recently, and with the appearance of multi-layer printed circuit boards (MLBs), electroless copper plating is being utilized to provide a connection between the surface of the substrate and the different layers of the board. However this technique results in a certain number of problems, particularly with a low plating rate or use of strong reducing agents such as formaldehyde (HCHO) (Gan *et al*. 2007). Research work has been implemented at the Sonochemistry Centre at Coventry University to examine the effect of ultrasound on the surface treatment of a few polymeric materials that are widely used within printed circuit boards and multi layer board manufacture, such as epoxy materials (Cobley and Mason 2007). After optimisation of the sonochemical process, a rough surface of the substrate epoxy material resulted which secured good adhesion between the epoxy and the subsequent electroless copper plating. The depth of copper plating within the holes of the printed circuit board was also examined (Cobley, Mason and Robinson 2008)) in order to determine if copper could be introduced between layers of a multi layer board when employing ultrasound at 20 kHz frequency. The results obtained in this study showed that ultrasonically dispersed copper nanoparticles could be used as a catalytic layer for through hole electroless deposition. “Although the coverage achieved in this study was not as good as with a standard palladium catalysed sample, it was significantly better than the mechanical agitation that was used to disperse the copper nanoparticles" (Cobley, Mason and Robinson 2008)

## 1.5 Analytical equipment

### 1.5.1 Weight Gain

Weight gain is a simple procedure employed to determine the amount of copper that has been deposited on the surface of materials of such as polymers and plastic (Coombs 1988). It has been used in traditional electroless copper plating in printed circuit board manufacturing (Coombs 1988) for many years. The weight gain method utilizes an electronic balance (figure 9) by weighing substrates three times before and after electroless copper plating is applied. It is a standard Industrial method which has also been employed by researchers such as Cobley (2010) and Touyeras *et al.* (2005).

This item has been removed due to third party copyright. The unabridged version of the thesis can be viewed at the Lanchester library, Coventry University.

Figure (9) Electronic Balance (ECVV 2011)

### 1.5.2 Gloss Meter

Gloss is measured by using a Gloss meter (figure 10). This measurement is essential where an appearance of plating finish is required. A Gloss meter is a device that measures the reflected light from the substrate surface. The gloss measurement is utilized to confirm the physical changes on the surface of materials after treatment and also measures the smoothness of the surface. A brighter shinier surface indicates a smoother surface and a more even electroplated coating with finer grain sizes which results in a high gloss reading.

Figure 10, Stargloss Glossmeter (Tonanasia 2009)

### 1.5.3 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that produces images of the sample surface by scanning it with a high-energy beam of electrons instead of using light (Mkhlef 2010). Samples have been examined with the SEM using two magnification options (1000 times and 10,000 times) in order to show the best image of the substrate surface. After surface plating with the copper, a thin layer of copper is then deposited on the surface of the material to enable SEM analysis. Samples are then viewed using a Jeol JSM-6060LV SEM. There are a few advantages of using this instrument including (i) it is considered an easy method to employ in order to observe the surface of the sample as long as this surface is conductive, (ii) the SEM has the ability to produce larger depth of focus for the sample surface, and (iii) the images that are produced by this instrument have greater resolution and very high magnification with a three dimensional appearance which gives a useful understanding of the sample surface. All these advantages make this instrument a widely used device by many researchers such as Touyeras *et al.* (2005) and Mandich (1994).

Figure (11) Epoxy surface at Silent condition        Figure (12) Epoxy surface at 500 kHz

Figures (10) and (11) (Touyeras *et al.* 2005)

### 1.5.4 X-ray Photoelectron Spectroscopy (XPS):

X-ray photoelectron spectroscopy (XPS), which is also known as an electron spectroscopy for chemical analysis (ESCA), is used widely in many industrial applications such as catalysis, adhesion, polymer surface modification, thin film coating, electronics packaging and surface analysis techniques (Briggs 1998). The wide use of this instrument is attributed to its relative simplicity of use and data analysis. The samples that are to be analyzed are irradiated with mono-energetic X-rays, which then release photoelectrons from the sample surface. An electron energy analyzer is fitted within this instrument which is then able to determine the binding energy of the photoelectrons released from the samples surface. It is known that a specific binding energy is associated with each core atomic orbital for each element (Briggs 1998). Therefore, the binding energy and intensity of the photoelectron peak can indicate the presence of a specific element within the sample being studied.  Thus the chemical state and element identity can be determined by this instrument which provides quantitative analysis of the surface composition (Fadley 2010).

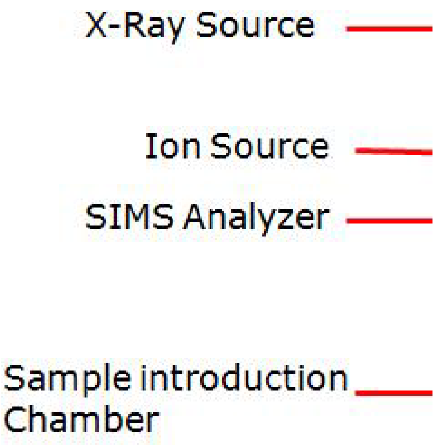


Figure 12, X-ray photoelectron spectroscopy (XPS) analyser, (MMRC n.d.)

XPS was used to demonstrate whether Pd was removed from the substrate surface when ultrasound was applied by measuring the amount of Pd on the substrate surface. The copper plating solution was used for XPS experiments but was utilized without any copper containing component see section (2.10.5).

# 2. EXPERIMENTAL

## 2.1 MATERIALS

Epoxy Tg resin (supplied by Isola)

## 2.2 CHEMICALS

1. Circuposit Conditioner 3323-A (Monoethanolomine 141-43-5, Triethanolamine 102-71-6, Water 7732-18-5) supplied by CHESTECH.
2. Circuposit Pre-dip 3340-4400 (Sodium bisulfate 76, Carbamidic acid, Chloride compound) supplied by CHESTECH.
3. Circuposit Catalyst 3344-4444 (Hydrogen Chloride 7647-01-0, Stannous Chloride 7772-99-8) supplied by CHESTECH.
4. Circuposit Copper 3350 A-1 (Copper Chloride 7447-39-4, Water 7732-18-5) supplied by CHESTECH.
5. Circuposit 3350-R1 (Water 7732-18-5, Tetrasodium salt of Ethylenediaminetetraacetic acid (EDTA), Tetrahydrate 64-02-8, Pyridine compound) supplied by CHESTECH.
6. Circuposit 3350 M-1 Ethylenediaminetetraacetic acid (EDTA) supplied by CHESTECH.
7. Formaldehyde solution 36.5% ($CH_2O$) supplied by Sigma-aldrich.
8. Sodium Hydroxide 77% (NaOH) supplied by Acros Organic.
9. Sulfuric Acid 98% ($H_2SO_4$) supplied by Fisher.
10. Glyoxylic Acid 50% ($C_2H_2O_3$) supplied by Acros Organics.
11. Sodium Sulfite ($Na_2O_3S$) supplied by Sigma- Aldrich.
12. Sodium Acetate Trihydrate ($C_2H_3NaO_2 . 3H_2O$) supplied by Sigma- Aldrich.
13. Acetic Acid ($CH_3COOH$) supplied by AR Fisons.

## 2.3 EQUIPMENT

1. Sonic system bath frequency 40 kHz (Sonic processor P100)
2. Sonic system bath frequency 850 kHz (Sonic processor)
3. Sonic system probe frequency 20 kHz (Sonic processor P100)
4. Four figure balance BDH (AA-250) weight was used to calculate the weight gain
5. Oven (Heraens instruments) was used to dry the test pieces before and after plating process
6. Timer (Fisher scientific) was used to control the process time

## 2.4 DETERMINATION OF THE ACOUSTIC POWER

### 2.4.1 Calorimetry

#### 2.4.1.1 Calorimetry measurement using probe 20 kHz

200 mL of RO water (reverse osmosis filtered water) was taken in a 400 mL beaker and sonicated with a 20 kHz probe at three different settings (30, 40 and 50%). The temperature (T) was monitored using a thermocouple at 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 seconds (t). The probe was positioned about half depth (6 cm) in the water. This position was recorded and was used again for the subsequent experiments. The experiment was repeated two times and an average value of Power (Watts) and Intensity (W/cm$^2$) was calculated.

#### 2.4.1.2 Calorimetry measurement using bath 40 kHz

200 mL of RO water was taken in 400 mL beaker and sonicated with (40 kHz bath 475TT) at specific power settings, and the temperature (T) was monitored at 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 seconds (t, the time). The beaker was positioned at 8 cm depth within the bath. This position was recorded and was used again for subsequent experiments. The water was replaced and the experiment was repeated two times at the same power setting and the average value of Power (Watts) and Intensity (W/cm$^2$) was calculated.

#### 2.4.1.3 Calorimetry measurement using bath 850 kHz

200 mL of RO water was taken in 400 mL beaker and was sonicated with (850 kHz bath) at specific power settings, and the temperature (T) was monitored at 0, 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150 and 180 seconds (t). The beaker was positioned at 8cm depth within the bath. This position was recorded and used again for subsequent experiments. The water was replaced and the experiment was repeated two times at the same power setting and the average value of Power (Watts) and Intensity (W/cm$^2$) was calculated.

### 2.4.2 Dosimetry

#### 2.4.2.1 Potassium Iodide Dosimetry

200 mL of 4% w/v solution of potassium iodide was taken (4 g KI in 95 mL of distilled water plus 2 mL 5% $H_2SO_4$ and this was then placed in a 500 mL beaker and stored in a dark and cool place to prevent air oxidation). Ultrasound was applied by using 40 kHz, 850 kHz and 20 kHz with a different power settings (20%, 30%, 40% and 50%). The temperature was maintained at $20^{o}C$. 5 mL aliquots were removed at 0, 10, 20 and 30 minutes. The absorbance of the solution was measured at 355 nm by using a UV spectrophotometer, using 2% aqueous KI in the reference cell and a calibration plot was used to determine the Potassium Iodide concentration.

Preparation of Potassium Iodide Calibration Plot

The calibration plot is constructed by first preparing a series of solutions from a stock of 4% acidified aqueous (4 g KI in 100 mL in distilled water plus 5 mL 0.5M $H_2SO_4$). To each of six 10 mL volumetric flasks was added 5 mL of the KI Solution followed by different quantities of the standardized $H_2O_2$ (0, 1, 2, 3, 4, 5 mL). Each solution was then made up to 10 mL with distilled water. The solutions were shaken and left for 15 minutes in the dark to ensure complete reaction.

The absorbance of each solution was recorded at 355 nm using 2% aqueous KI in the reference cell. The absorbance plotted against concentration of $H_2O_2$ had given a very good straight –line (Beer-Lambert) calibration plot.

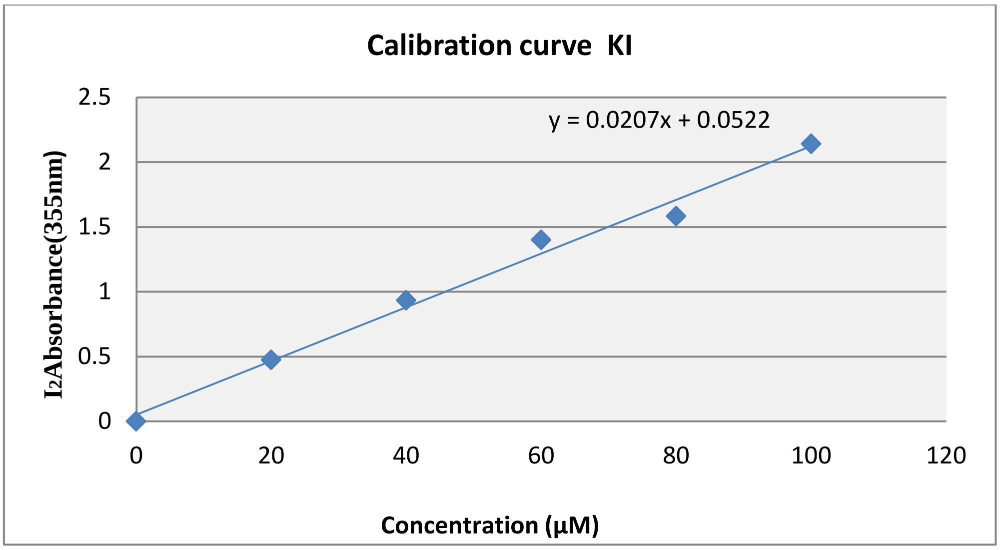


Figure 13 Calibration curve produced by KI

The amount of hydrogen peroxide present can be calculated from the absorbance of iodine given that the chemical reactions occurring follow the following stoichiometric equation.

$$H_2O_2 + 2\,KI + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2\,H_2O$$

Therefore employing the calibration curve for iodine formation (Fig 13 above) can be a direct measure of how much hydrogen peroxide is present in the solution.

### 2.4.2.2 Nitrophenol Dosimetry

A master 4-nitrophenol solution was prepared from 0.278 g of 4-nitrophenol which was added to 2 litres of distilled water and lowered to pH 5 with (HCl 1%). 20 mL of this solution was taken and added to 180 ml of water. This diluted solution was used to run the experiment. 200 mL of the diluted 4-nitrophenol solution was prepared and placed in a 500 mL beaker. Ultrasound was then applied (40 kHz, 850 kHz and 20 kHz). The temperature was maintained at 20 °C. 5 ml samples were taken at 0, 15, 30, 45 and 60 minutes. Prior to spectrophotometer (UV-7520) analysis these samples were diluted with 5 ml of 0.2 M NaOH, in a small beaker then 2 mL of this solution was put in the reference cell and the absorbance was measured at 401 nm. This was repeated 3 times.

The absorbance of each solution was recorded at 512 nm using (2%) aqueous 4-nitrophenol in the reference cell. The absorbance plotted against concentration of 4-nitrophenol had given a very good straight –line (Beer-Lambert) calibration plot.

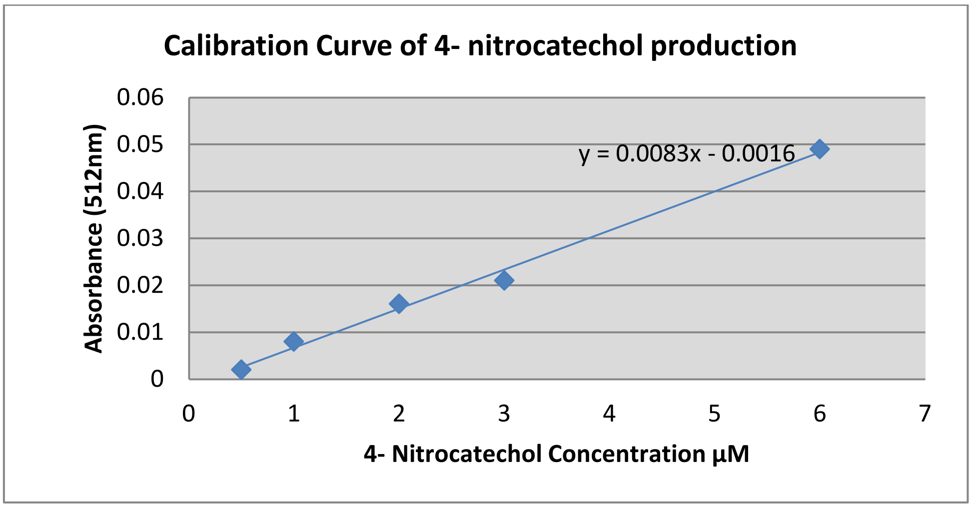


Figure 14 Calibration curve for 4-nitrophenol dosimetry

Using the gradient from Figure 14 the concentration of4-nitrocatechol could be calculated from the absorbance at the different time intervals using the equation:

$$Concentration\ of\ 4 - Nitrocatechol = (x + 0.0016)/0.0083$$

$x$ represents the absorbance of 4-Nitrocatechol at a specific time period. The values 0.0083 and 0.0016 represent the gradient and are used to calculate the concentration from the absorbance.

### 2.4.2.3 Methyl Orange Dosimetry

200 mL of 10µM methyl orange solution (5 g/L) was placed into a 400 mL beaker then ultrasound of frequencies 40 kHz and 850 kHz were applied using 40 kHz bath and 850 kHz bath. The temperature was kept at 20°C by using ice with the 40 kHz bath and a cooling system with the 850 kHz bath. 5 mL aliquots were removed at times of 0, 15, 30, 45, 60 min. The absorbance of the solutions was measured at 464 nm using a UV/visible spectrophotometer (UV-1650PC Shimadzu) and referenced against RO water. Samples were measured at the wavelength range of 200-600 nm to determine λmax.

The selected wavelength for determining the methyl orange decolourisation was 464 nm. All the tests were repeated three times. Calibration was performed by making standard dilution of the 10 µM methyl orange solution in RO water and analyzing at 464 nm.

The absorbance of each solution was recorded at 464 nm using (2%) aqueous methyl orange in the reference cell. The absorbance plotted against concentration of methyl orange has introduced a very good straight – line (Beer-Lambert) calibration plot.

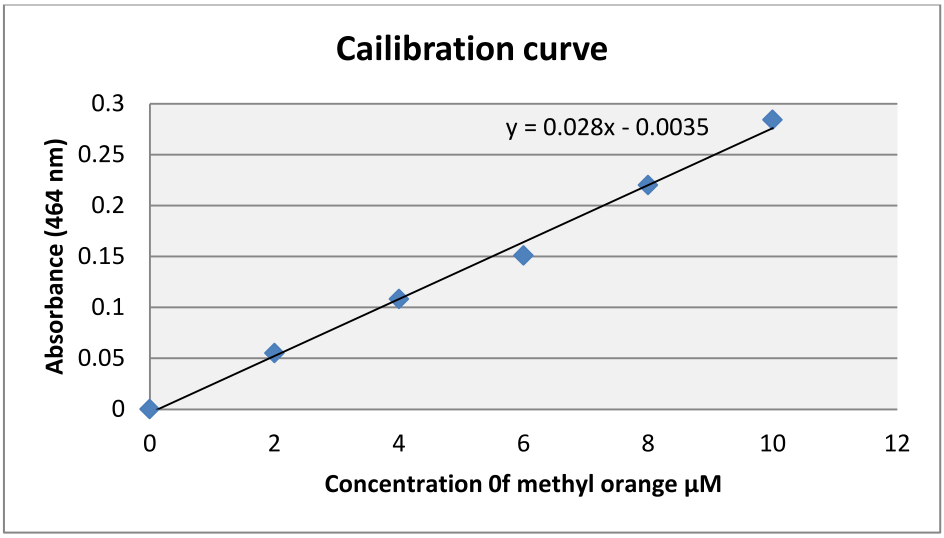


Figure 15 Calibration curve for Methyl Orange Dosimetry

## 2.5 Electroless copper plating

### 2.5.1 Solutions for Conventional Electroless Copper Plating

The Electroless copper plating process in this study required three chemical solutions i.e. conditioner, catalyst, and copper solution. These chemicals are used in the conventional electroless copper plating process within the manufacturing printed circuit boards for the last 40 years. These solutions were prepared as follows:

1- **Conditioner solution:**

Table (1) Conditioner Solution Composition

| **Component** | **Volume** |
|---|---|
| RO water ($H_2O$) | 980 mL |
| Circuposit Conditioner | 20 mL |

2- **Catalyst solution:**

Table (2) Catalyst Solution Composition

| **Component** | **Volume** |
|---|---|
| RO water ($H_2O$) | 450 mL |
| Circuposit Pre-dip 3340/4400 | 270g/500 mL |
| Circuposit catalyst 3344/4444 | 30 mL |

3- **Copper solution:**

Copper solution (1000 ml) which is used with 40 kHz

Table (3) Copper Solution composition

| **Component** | **Volume** |
|---|---|
| D.W distilled water ($H_2O$) | 807 mL |
| EDTA ($C_{10}H_{16}N_2O_8$) | 150 mL |
| copper(II) chloride ($CuCl_2$) | 10 mL |
| Sodium hydroxide (NaOH) | 23.5 mL |
| Formaldehyde ($CH_2O$) | 10 mL |

### 2.5.2 The Conventional electroless copper plating process

The nonconductive substrate used in all experiments was a 30 x 30 x 1 mm epoxy resin plate. Four samples were immersed in 1 L of Circuposit Conditioner (20 mL /1 L) at 50 $^{o}$C for 5 minutes and water rinsed for 4 minutes beneath a tap. The samples were then immersed in a 1 L beaker containing both Circuposit pre-dip (270 g/ L) and Circuposit Catalyst (30 ml/ L) at 40 $^{o}$C for 5 minutes and water rinsed for 4 minutes beneath. The samples were the immersed in 1 litre of copper solution (10 ml copper chloride/litres) for 25 minutes at different temperatures (25, 30, 35, 40, 45 and 50 $^{o}$C) and then water rinsed for 2 minutes beneath a tap. Finally the samples were then placed in the oven at 90-100 ºC for 24 hours. Each experiment was repeated two times. Figure (14)

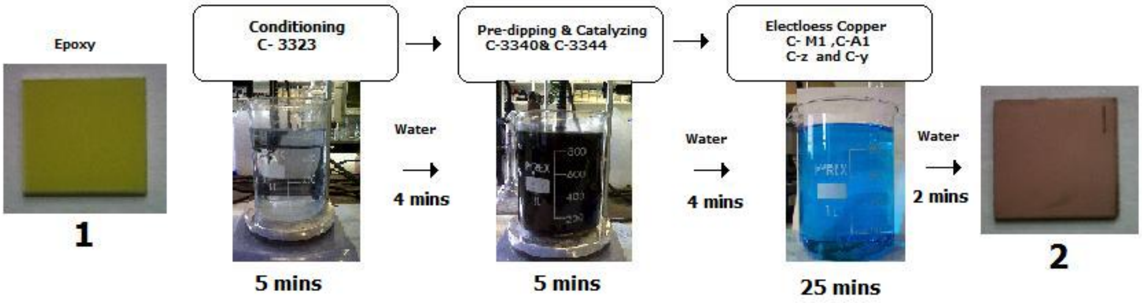


Figure (16) Electroless copper plating procedure

After the samples were dried, different analysis methods were performed including, weight gain, scanning electron microscope and gloss meter readings.

The electroless copper plating bath was also analyzed after each procedure and replenished (see Section 2.6).

### 2.5.3 The 40 kHz electroless copper plating process

The nonconductive substrate used in all experiments was a 30 x 30 x 1 mm epoxy resin plate. Four samples were immersed in 1 L of Circuposit Conditioner (20 mL /1 L) at 50 $^{o}$C for 5 minutes and water rinsed for 4 minutes beneath a tap. The samples were then immersed in a beaker 1 L containing both Circuposit pre-dip (270 g/ L) and Circuposit Catalyst (30 mL/ L) at 40 $^{o}$C for 5 minutes and water rinsed for 4 minutes beneath. The samples were the immersed in 1 L of copper solution (10 mL copper chloride/L) for 25 minutes and ultrasound was applied at a frequency of 40 kHz at different temperatures (25, 30, 35, 40, 45 and 50$^{o}$C) and samples were rinsed in the water for 2 minutes beneath a tap. Finally the samples were then placed in the oven at 90-100ºC for 24 hours. The experiment was repeated two times. After samples were dried, analysis methods were carried out by using weight gain, scanning electron microscope and the gloss meter.

### 2.5.4 The 850 kHz electroless copper plating process

The conditioner and catalyst solution that was used in 40 kHz experiments were used again in new experiments using 850 kHz frequency ultrasonic bath at different temperatures (25, 30, 35, 40, 45 and 50$^{o}$C). A different volume of electroless copper plating solution (250 mL) was used with 850 kHz because a beaker of 250 mL could not be placed inside the 850 kHz bath due to the small size of this bath. This solution was prepared as follows:

Table (4) Copper solution composition (250 ml)

| **Component** | **Volume** |
|---|---|
| RO water ($H_2O$) | 202 mL |
| EDTA ($C_{10}H_{16}N_2O_8$) | 37.5 mL |
| copper(II) chloride ($CuCl_2$) | 2.5 mL |
| Sodium hydroxide (NaOH) | 5.5 mL |
| Formaldehyde ($CH_2O$) | 2.5 mL |

## 2.6 Stability test of electroless copper solution

The spectrophotometer (UV-1800 Shimadzu) was used to measure the stability of the electroless copper solution for each electroless copper bath employed. The copper plating bath consisted of distilled water 80.7%, EDTA 15%, sodium hydroxide 2.3%, formaldehyde 1% and copper(II) chloride 1%. The plating process was carried out as following the normal general plating processes (see section 2.5). After this process (2.5mL) was then taken from the electroless copper solution after the plating process and then put in a small beaker (100-150 mL) and mixed with (5 mL) buffer solution to keep a constant pH for this solution. After it was well mixed, 3 ml from this solution was put in a plastic cuvette to measure the absorbance of the solution at 730 nm and compared to distilled water. This process was repeated three times after the first and second use, and then after 24 hours to determine the bath stability. The levels of copper present in the solution where determined by comparison to the bath copper levels at time zero. The percentage of copper in the elctroless copper solution was calculated as follows:

$\frac{Abs\ of\ Bath}{Abs\ of\ STD\ \ A}$ *x 100 = Percentage copper* ………….. Eq. 5

or

$\frac{Abs\ of\ Bath}{Abs\ of\ STD\ A}$ *x 2.0 = g/L copper* ……………….Eq. 6

Note: STD A = electroless copper bath at time zero

Depending on the copper concentration found in the electroless copper solution, the bath was replenished according to the following table:

Table (5) Bath replenishment conditions

| % Copper Concentration | g/L copper concentration | Remove (mL) | Add C 3350 Copper(II) Chloride A-1 (mL) | Add C 3350 R-1 (mL) | Add Sodium hydroxide (NaOH) (mL) | Add Formaldehyde ($CH_2O$) (mL) |
|---|---|---|---|---|---|---|
| 100 | 2.0 | --- | --- | | | |
| 90 | 1.8 | 0.8 | 0.10 | 0.075 | 0.23 | 0.15 |
| 80 | 1.6 | 1.6 | 0.20 | 0.15 | 0.46 | 0.30 |
| 70 | 1.4 | 2.4 | 0.30 | 0.225 | 0.69 | 0.45 |
| 60 | 1.2 | 3.2 | 0.40 | 0.30 | 0.92 | 0.60 |

## 2.7 Air bubbling experiments

All experiments were performed using the same steps above as sections (2.5.2, 2.5.3 and 2.5.4) but with air inside the copper solution, introduced by using an air pump. Ultrasound was applied for 25 minutes but with an initial time delay introduced during the copper plating process. Air was applied by using an air pump with a 120 L/h flow rate using a glass tube for 25 minutes during the electroless copper bath/stage only. Figure (15)

Figure (17) Experimental set up for air bubbling experiments

## 2.8 Glyoxylic acid as a reducing agent

All experiments were performed using the same steps in sections 2.5.2 and 2.5.3 under silent conditions and also 40 kHz and 850 kHz sonication. Glyoxylic acid replaced formaldehyde as the reducing agent. A solution of glyoxylic acid was prepared (the molarity of this solution was equivalent to the molarity of formaldehyde reducing agent that was used in the previous experiments). As a result, 6.25 mL of 50% glyoxylic acid was added to the electroless copper bath.

## 2.9 Delays in Sonication

All experiments were performed using the same steps as sections 2.6, 2.7, and 2.8 with 40 kHz and 850 kHz. However introducing a different delay time (2, 4, 7 and 10 minutes) before the ultrasound was turned on. The pre-treatment times were as follows:

Table (6) Indication of delay times applied during sonication

| Total plating time (minutes) | Stand by time (minutes) | Ultrasound on (minutes) |
|---|---|---|
| 25 | 0 | 25 |
| 25 | 2 | 23 |
| 25 | 4 | 21 |
| 25 | 7 | 18 |
| 25 | 10 | 15 |

## 2.10 ANALYSIS

### 2.10.1 Weight gain

Weight gain is an easy process for calculating the amount of surface coating of copper. The weight of each epoxy Tg resin sample was recorded before the electroless copper plating was applied and the weight gained for each sample was recorded three times after the electroplating processes. This was repeated three times

The amount of sample weight gain was calculated as follows:

$$\text{Weight gain (g)} = \text{Weight after treatment (g)} - \text{Weight before treatment (g)} \quad \text{Eq. 7}$$

This equation was used to calculate the ratio of weight gain according to the area of each sample and for both faces of the substrate.

Then calculate: *Thickness in 25 minutes*

$$T = \frac{\Delta M}{P * Area} \quad \text{…………. Eq. 8} \qquad T = \text{Thickness} \quad \frac{g}{\frac{g}{cm3}\, x\, cm2} = cm$$

$\Delta M$ = *Weight gain g*

$P$ = *Copper density* $g/cm^3$

*Area of sample =* $cm^2$

*Plating rate µm = Thickness cm /25minutes*

### 2.10.2 SEM Scanning Electronic Microscope

After electroless copper plating, samples from each experiment were dried in the oven for 24 hours to enable SEM analysis. Samples were tested using a Jeol JSM-6060LV SEM. A photograph was taken at particular magnification (1000 and 10,000 times), and the texture of the surface was assigned by grading the photograph from 0-10. The grain structure size were graded as follows: (0 indicates a finer grain structure (eg. smooth surface) while 10 indicates a large grain structure (eg. extreme change in surface morphology).

An example scale to show how the pictures were assessed visually for epoxy (Tg resin) is shown as follows:

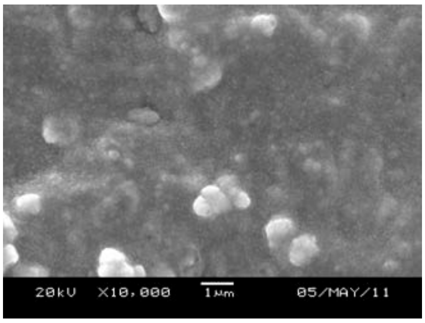
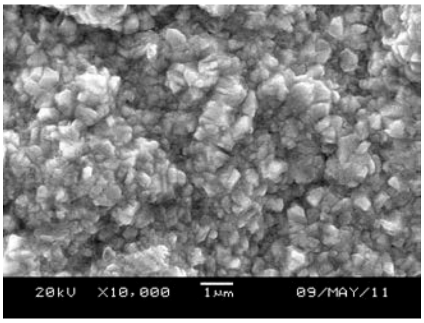
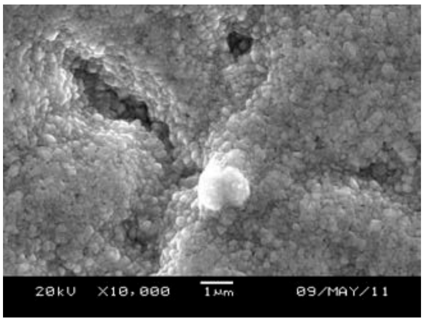
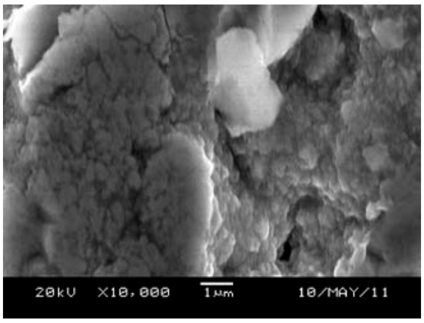
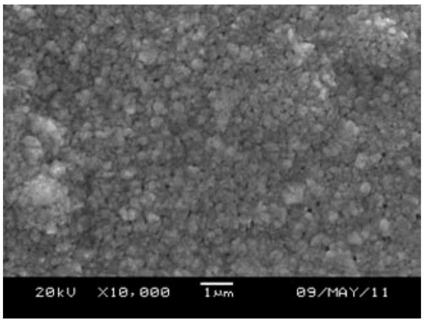
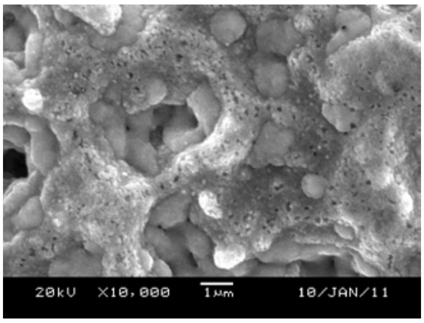
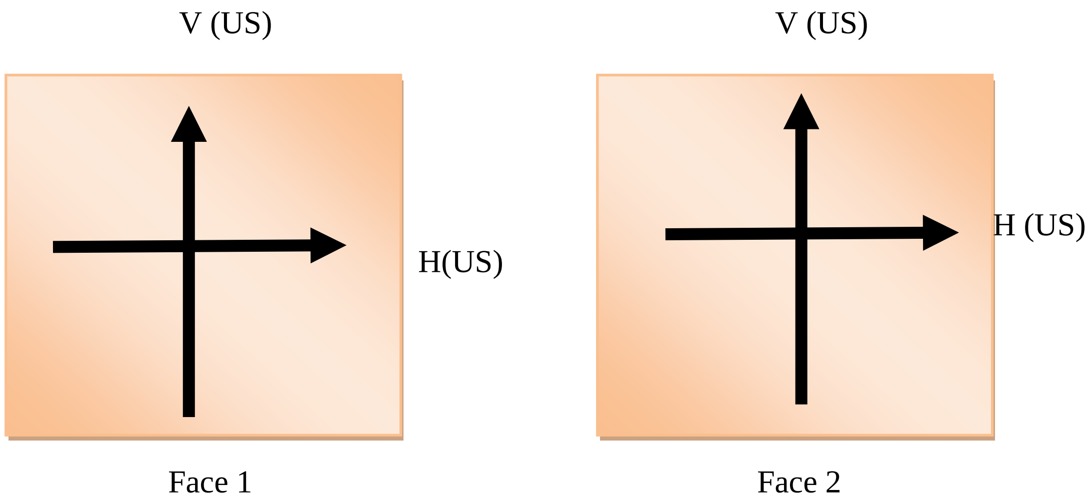
| Picture Grade (0-10) | Picture as shown by SEM | Picture Grade (0-10) | Picture as shown by SEM |
|---|---|---|---|
| **0** |  | **6** |  |
| **2** |  | **8** |  |
| **4** |  | **10** |  |

**Table (7) SEM pictures assessment scale**

### 2.10.3 Gloss Meter

The apparatus that was used in this method was a Stargloss Glossmeter at 60° angle. A high reading (reflectance of more light) suggests a smooth surface whilst a low reading (reflectance of less light) refers to a rough surface. The measurement was performed by taking four readings for each sample and for both sample faces as follows:



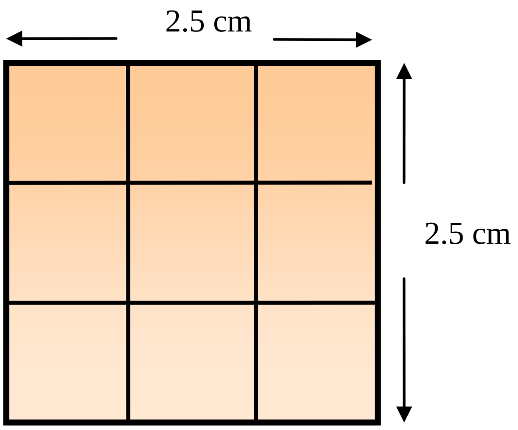
Face 1

Face 2

Figure, 18 Depiction of gloss meter measurement direction
(V and H refer to direction of ultrasound effect, vertical and horizontal)

### 2.10.4 Adhesion

The reason for carrying out electroless copper plating at low temperature on the epoxy substrates is to improve the degree of adhesion and for this reason, the treated samples were electroless copper plated and then the tape test was utilized to determine the bond strength (adhesion) between the copper coating layer and the epoxy substrate surface (Cobley and Mason, 2007). A cross-hatch grid was cut into the surface of the test sample using a sharp tool as follows:



Figure, 19 Drawing of adhesion test sample surface grid

The tape then was stuck to the surface of the epoxy and pulled from the surface strongly. All samples were graded qualitatively from 0-10. These numbers indicate the copper levels that have been adhered to the surface. Grade 10 indicates good adhesion (no copper was removed) while 0 grade indicates that the entire coat was removed.

### 2.10.5 XPS Analysis of Substrate

In this experiment, 5 epoxy test pieces were processed using the conditions as below. These were sent for XPS analysis to Loughborough Surface Analysis Limited (LSA Ltd). The solutions (1 to 3) used in these experiments can be found in section 2.5.1 above

Sample 1 – Conditioner (solution 1)/ Catalyst (solution 2)
– Dry

Sample 2 - Conditioner / Catalyst / Copper plating (solution 3) (With no copper)
– 4 minutes Silent

Sample 3 - Conditioner / Catalyst / Copper solution (with no copper)
– 4 minutes Ultrasound

Sample 4 - Conditioner / Catalyst / Copper solution (with no copper)
– 10 minutes Silent

Sample 5 - Conditioner / Catalyst / Copper solution (with no copper)
– 10 minutes Ultrasound

The copper containing component of the electroless solution was not added to the bath to prevent it from plating. These experiments were designed to demonstrate whether Pd was removed from the substrate surface when ultrasound was applied. The copper plating solution 3 (see section 2.5.1) was used for these experiments but was utilized without the copper containing component. This was to prevent the epoxy test coupons plating with copper, which would have masked the underlying Pd during XPS analysis.

# 3. Results and Discussion

## 3.1Determination of Acoustic Power

### 3.1.1 Calorimetry

Calorimetry is used as a physical technique to estimate the ultrasonic acoustic energy (ultrasound power) of ultrasonic equipment (Mason 1999). Calorimetric measurements of ultrasonic devices are performed for a few reasons such as (i) to ensure the compatibility in terms of power settings for different ultrasonic systems (ii) to ensure that ageing and erosion of the transducer has no effect on changing the performance of ultrasonic devices (iii) to get a rough estimate of ultrasonic intensity (often reported as W/cm$^2$) and energy density (reported as W/cm$^3$) in the solution under the conditions used.

The theory for calorimetry measurement is that when a liquid (such as water) is being sonicated, the liquid temperature increases and this can be recorded against the time by using a thermocouple, which is placed in the sonicated solution. From the (Temperature vs Time / second) plot the temperature rise at zero time, (*dT/dt*) can be estimated by either construction of a tangent to the curve at time = 0, or by curve fitting the data to a polynomial in *t*. The ultrasonic power actually entering the system can be determined by substituting the value of the change in temperature within the solution with respect to time (dT/dt), at time zero and by using the following equation.

$$\text{Power (W)} = (dT/dt)\, C_pM..... \qquad \text{Eq.9}$$

Where [Cp] is the specific heat capacity and [M] is the mass of water in each system. The specific heat capacity of water is 4.18 kJ/kg.K. The intensity can be calculated for each system by dividing the power applied by the volume used, or area of the tip of sonication probe, which gives:

$$\text{Intensity} = \text{Power (W)/ Area (cm}^2\text{)......} \qquad \text{Eqn.10}$$

Calorimetry has been utilized to determine the ultrasonic intensity (W/cm$^2$) within a 40 kHz and 850 kHz ultrasonic bath. After the calorimetric measurement, the equations above were used to calculate the ultrasonic intensity ($W/cm^2$). The results are as follows:

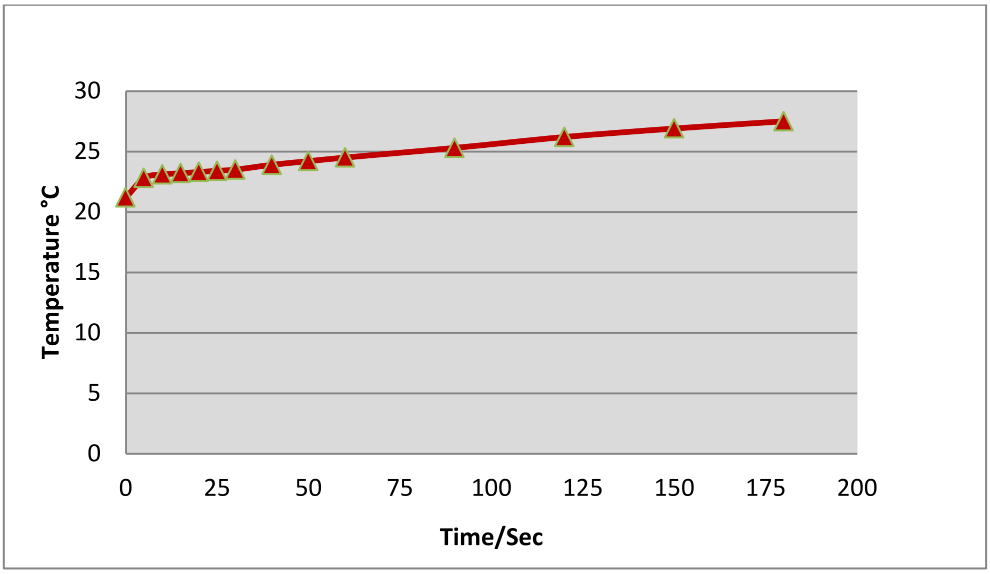


Figure (20) Calorimetry measurement results using a 40 kHz ultrasonic bath

Power (Pw) = (dT/dt) x Cp x M

=0.0222 x 4.18 x 200

= 18.5 Watt (W)

Intensity = Power/ Area

Area= $radius^2$ x π

= $(3.5)^2$ x 3.14= 38.46 $cm^2$

Intensity= 18.50/38.46= 0.48$W/cm^2$

The calorimetry measurement results that have been obtained by using the 40 kHz ultrasonic bath are exhibited in figure (20). All results have shown that the temperature has increased with an increased time of sonication. More cavitations are produced when more time is applied, which increases the temperature of the sonicated solution due to the collapse of the microbubbles and this collapse produces very high temperatures that could reach up to 5000ºC (Mason 1999). The other reason behind this increase in the temperature could be because more acoustic energy is absorbed via the solution when the sonication time is increased.

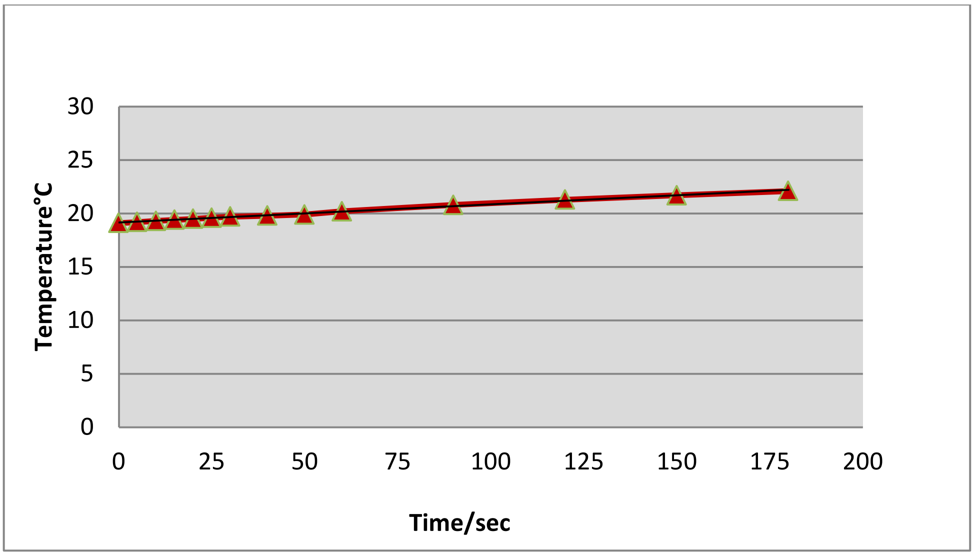


Figure (21) Calorimetry measurement results using an 850 kHz ultrasonic bath

Power (Pw)= (dT/dt) x Cp x M

=0.0196 x 4.18 x 200

= 16.38 watt (W)

Intensity = Power/ Area

Area= radius$^2$ x $\pi$

= $(3.5)^2$ x3 .14= 38.46 cm$^2$

Intensity= 16.38/38.46= 0.42W/cm$^2$

The calorimetry measurement results obtained by using the 850 kHz ultrasonic bath are presented in Figure (21). Using the 850 kHz bath increases the temperature of the liquid as the temperature of any solution under sonication is increased because of the acoustic energy that is absorbed by the liquid (Mason and Peters 2002). There is clear evidence that the temperature is increased directly as the sonication time is increased. Increasing the sonication time produces more cavitation, which means that more microbubbles collapse in the liquid thus causing increased temperatures.

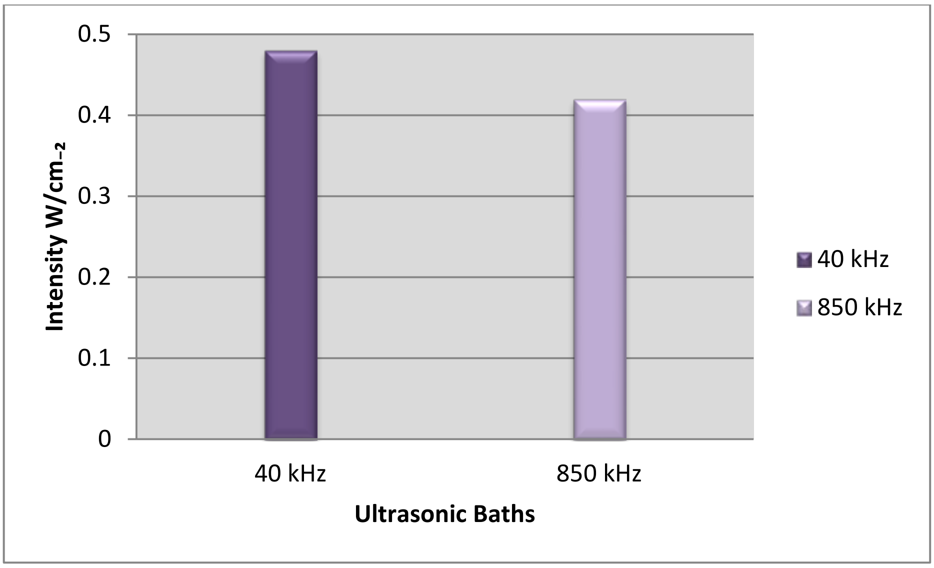


Figure (22) Intensity calculated for different baths

All the results obtained by utilizing the 40 kHz ultrasonic bath and the results obtained by using 850 kHz ultrasonic bath are summarised in Table (8).

Table (8) Power and intensity calculated for different frequencies

| Ultrasound source | Frequency(kHz) | Volume mL | Power setting % | Calculated power W | Intensity W/cm$^2$ |
|---|---|---|---|---|---|
| Ultrasonic Bath | 40 | 200 | Max | 18.5 | 0.48 |
| Ultrasonic Bath | 850 | 200 | Max | 16.38 | 0.42 |

Using the 40 kHz ultrasonic bath produced a higher temperature rise than the 850 kHz bath. At higher frequencies, microbubbles sizes are decreased and therefore the collapse temperature is decreased (Mason and Peter 2002). The results show that with the high frequency (850 kHz), the intensity decreased. As the frequency of sonication increases, the rarefaction cycle gets shorter and the power of sonication must be increased to maintain an equal level of cavitational energy within the system. Higher frequencies result in smaller cavitation bubbles than lower frequencies of ultrasound (Mason 1999). From the results it is clear that the 40 kHz bath produced the highest power and intensity.

### 3.1.2 Dosimetry

Calorimetry is used to determine the physical effect of ultrasound, particularly in terms of the actual power entering the sonicated solution whilst dosimetry is a chemical method to estimate the chemical effect of the ultrasonic devices by monitoring the production of free radicals. The chemical dosimetry method is based upon the fact that sonication of water produces radicals ($H^•$ & $OH^•$), which are involved in reactions and eventually form $H_2O_2$ (Mason 1999). Ultrasonic irradiation has been found to be extensively useful for the destruction of aqueous organic and inorganic pollutants. The substrate molecules can undergo degradation by two different main pathways depending on their chemical nature; pyrolytic reactions inside the cavitation bubbles or oxidation by hydroxyl radical in the bulk medium. The effect of ultrasound waves on hydrophilic chemical oxidation is due to the production of hydroxyl radicals during the cavitation-induced thermal decomposition of water.

In pure water, the initial homolytic fission of the O-H bond is followed by a whole series of other radical reactions (Mason and Peters 2002).

$H_2O \longrightarrow HO^• + H^•$

$H^• + O_2 \longrightarrow HO_2^•$

$2HO^• \longrightarrow H_2O_2$

$2\ HO_2^• \longrightarrow H_2O_2 + O_2$

$H_2O_2$ is well known for its oxidative nature. Its formation in water as a result of sonication could then allow it to be involved in further subsequent oxidation reactions with substrates found within the aqueous solution. Generally, chemical dosimetry is used to monitor the production of chemical species within the sonicated solution and to estimate the chemical energy of an ultrasonic device. Many experiments such as iodine dosimetry (Mason and Peters 2002), methyl orange dosimetry (Tanaka et al. 1999), and para-nitrophenol (Mason and Peters 2002), dosimetry are practiced.

The electroless copper plating process contains a reducing agent that starts the oxidation reaction on the catalyst substrate. Therefore, it is necessary to determine the hydroxyl free radicals generated in liquid due to the cavitation bubbles, which might affect the oxidation process occurring within electroless copper plating.

### 3.1.2.1 Potassium Iodide Dosimetry

The iodide dosimetry method is based upon the fact that the sonication of water produces $H_2O_2$ and this reacts quickly with $I^-$ in solution to release molecular iodine. Thus when aliquots of deionised water are added to KI solution, fixed quantities of iodide will be liberated and the yield of iodide can be estimated by the increase in absorbance of this species at 355 nm on a UV/visible spectrophotometer.

Potassium iodide can be oxidized by oxidative reagents in an aqueous system with ultrasound. The oxidative reagent is hydrogen peroxide, formed as a result of cavitational collapse. Applying the ultrasound into the water produces free radicals and these are involved in subsequent reactions and generate $H_2O_2$. It has been reported that when $H_2O_2$ is added to a KI solution, a known amount of iodine will be released, which can be estimated via the increase in absorbance of iodine. So, the rise of the iodine absorbance, or concentration, is actually the reflection of the increase in the $H_2O_2$ production (Mason 2002). The reaction equation is as follows:

$$2KI + H_2SO_4 + H_2O_2 \rightarrow I_2 + K_2SO_4 + 2H_2O$$

Table (9) Iodine absorbencies for different ($H_2O_2$) dilutions at 355 nm

| Concentration of $H_2O_2$ (µM) | $I_2$ UV Absorbance (355nm) |
|---|---|
| 0 | 0 |
| 20 | 0.472 |
| 40 | 0.933 |
| 60 | 1.399 |
| 80 | 1.582 |
| 100 | 2.14 |

Using the gradient from Figure 23 the concentration of $H_2O_2$ could be calculated from the absorbance at the different time intervals using the equation:

$$Concentration\ of\ \mathrm{H2O2} = (x - 0.0522)/0.0207$$

$x$ represents the absorbance of $I_2$ at a specific time period. The values 0.0207 and 0.0522 represent the gradient and are used to calculate the concentration from the absorbance.

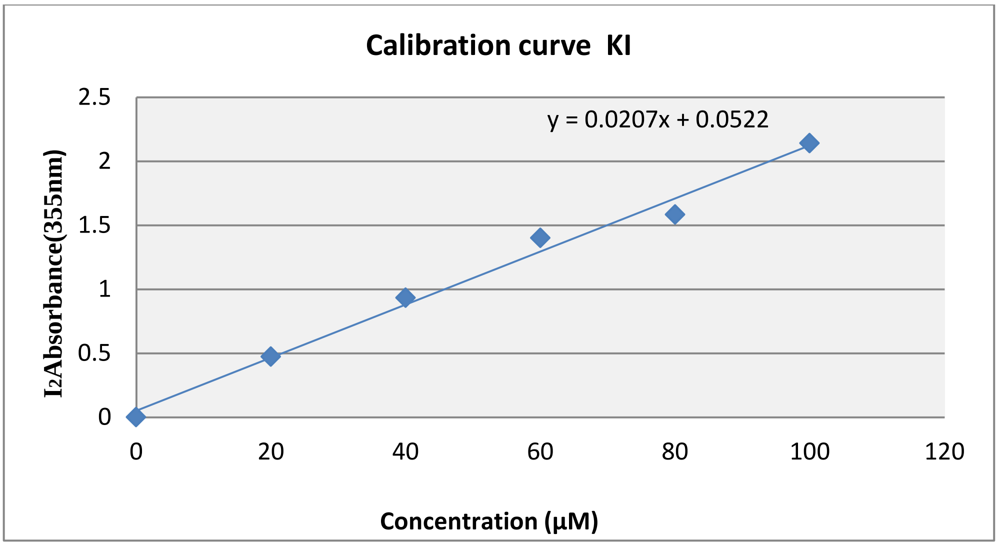


Figure (23) the absorbance of $I_2$ versus the concentration

The results show the calibration of potassium iodide that the $I_2$ absorbance (355nm) increased with increasing of concentration of KI, which indicates a positive relationship between concentration and absorbance. The rate of increase is almost constant (0.45) for each 20µM increase in concentration, which explains the increase in absorbance due to increasing the molecules of iodine dissolved in the solvent.

$$KI \xrightarrow[H_2O_2\ \text{production}]{\text{Ultrasound}} I_2$$

Therefore, on sonication, any ($I_2$) liberated will be as a direct consequence of $H_2O_2$ production from the application of ultrasound to the KI solution.

<u>40 kHz Bath</u>

The table and the figure below shows the data obtained from potassium iodide dosimeter using a 40 kHz bath.

Table (10) Data obtained from potassium iodide dosimety using a 40 kHz bath

| Time (min) | Absorbance of $I_2$ (355nm) | Concentration of $H_2O_2$ (µM) |
|---|---|---|
| 0 | 0.199 | 7.091 |
| 10 | 0.379 | 15.787 |
| 20 | 0.579 | 25.449 |
| 30 | 0.930 | 42.405 |

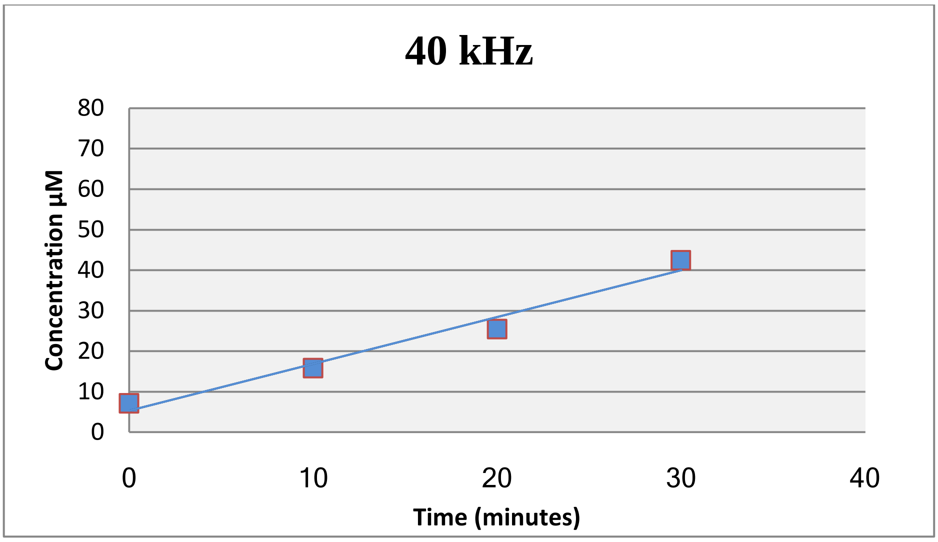


Figure (23) $H_2O_2$ concentration versus time using the 40 kHz ultrasonic bath

The results when using the 40 kHz bath show an increase in the $H_2O_2$concentration with increasing sonication time. The concentration increased because more cavitations are produced and more free radicals are generated (Mason 2002).

850 kHz Bath

The table and the figure below show the data obtained from potassium iodide dosimety using an 850 kHz bath.

Table (11) Absorbance of iodine over thirty minutes using 850 kHz

| Time (min) | Absorbance of $I_2$ (355nm) | Concentration of $H_2O_2$(µM) |
|---|---|---|
| 0 | 0.138 | 4.144 |
| 10 | 0.459 | 19.652 |
| 20 | 0.863 | 39.169 |
| 30 | 1.312 | 60.8599 |

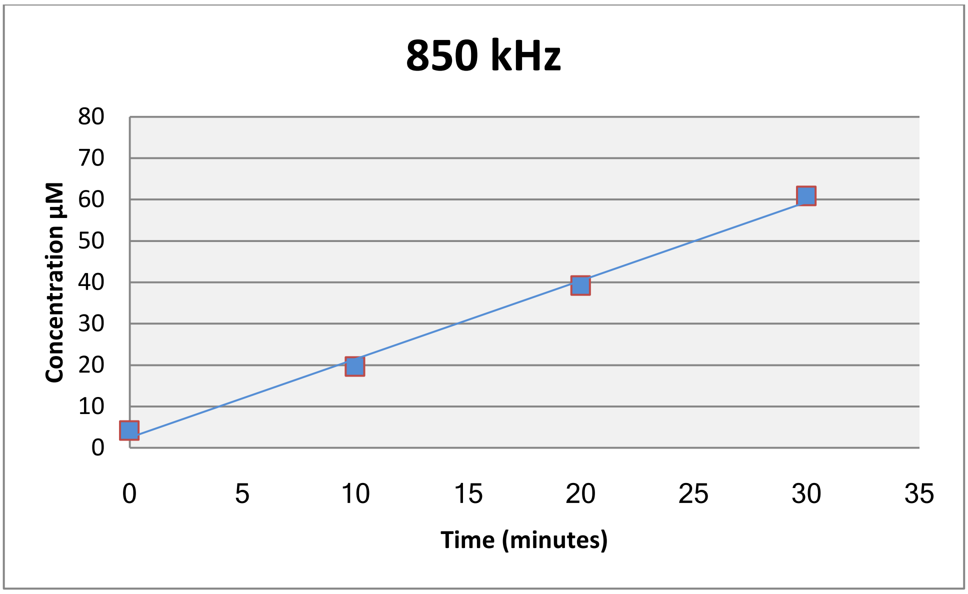


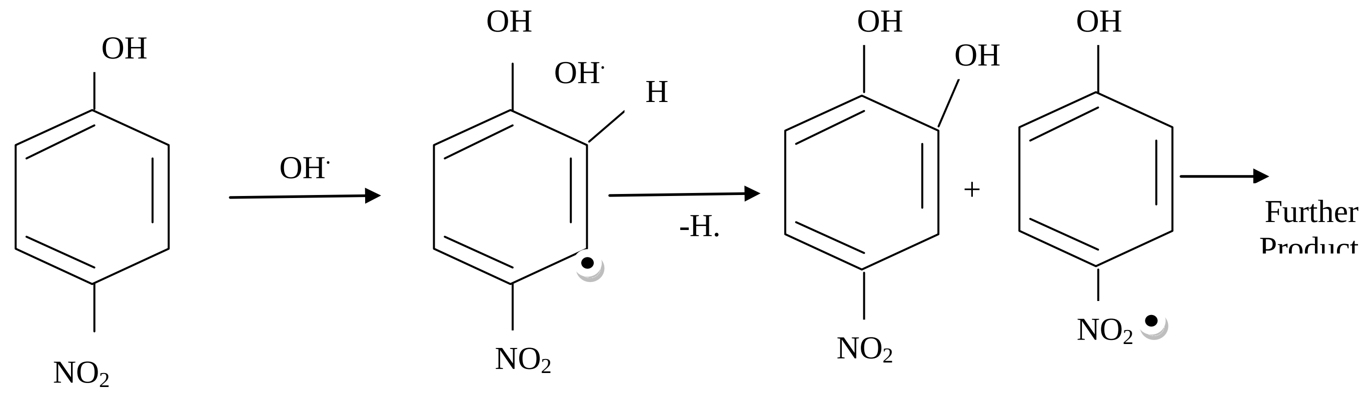
Figure (24) $H_2O_2$ concentration versus time using the 850 kHz bath

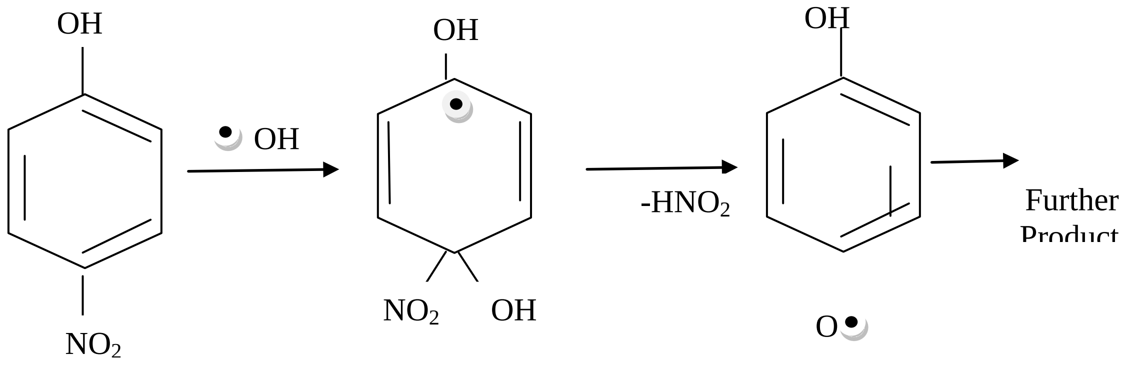
The concentration of the $H_2O_2$ increased with time, which indicated that more free radicals are generated and this means that more cavitations are produced (Mason 2002). All the results have shown an increase in the $H_2O_2$ concentration with increase of the sonication time. This is attributed to the more microbubbles that are formed when more sonication time is applied and more free radicals in the solution. Using the 850 kHz ultrasonic bath introduced higher concentrations of hydrogen peroxide than the concentrations obtained with 40 kHz ultrasonic bath. At higher frequencies, more radicals are generated and this increases the concentration of the $H_2O_2$ (Mason and Peters 2002). It has been stated that at higher frequencies, the collapse of the bubbles occurs more rapidly and more free radicals escaped from the bubbles into the bulk solution (Mason and Peters 2002)

### 3.1.2.2 Nitrophenol Dosimetry

The theory of p-nitrophenol dosimetry is similar to iodide dosimetry. The p-nitrophenol is oxidized by the hydroxyl $OH^{\bullet}$ which is produced due the generation of the free radicals by the application of ultrasound; these radicals are formed because of cavitation. The production of $OH^{\bullet}$ can be estimated by monitoring the production of the hydroxylated compound (ortho-catechol). Indeed, the nitrophenol dosimeter is specific for $OH^{\bullet}$ rather than potassium iodide as this measures the production of the total formation of the free radicals (Mason 2002).

The reaction is illustrated as following:





The p-nitrophenol-dosimeter uses the oxidation of p-nitrophenol (PNP, 4-nitrophenol) and the reaction is monitored photometrically. Aqueous PNP has an ultraviolet maximum at 401 nm and hydroxylated product at 512 nm. It is therefore possible to quantify the number of hydroxyl radicals formed during sonication by observing the amount of product that has been formed (Mason 2002).

The absorbance of the product the hydroxylated compound (4-nitrocatechol) was measured at 512 nm to determine the concentration of the free radicals $OH^{\bullet}$.

Table (12) Concentration versus Absorbance of 4-nitrocatechol

| Concentration of 4-nitrocatechol (µM) | Absorbance of 4-nitrocatechol at 512 nm |
|---|---|
| 0.5 µM | 0.002 |
| 1 µM | 0.008 |
| 2 µM | 0.016 |
| 3 µM | 0.021 |
| 6 µM | 0.049 |

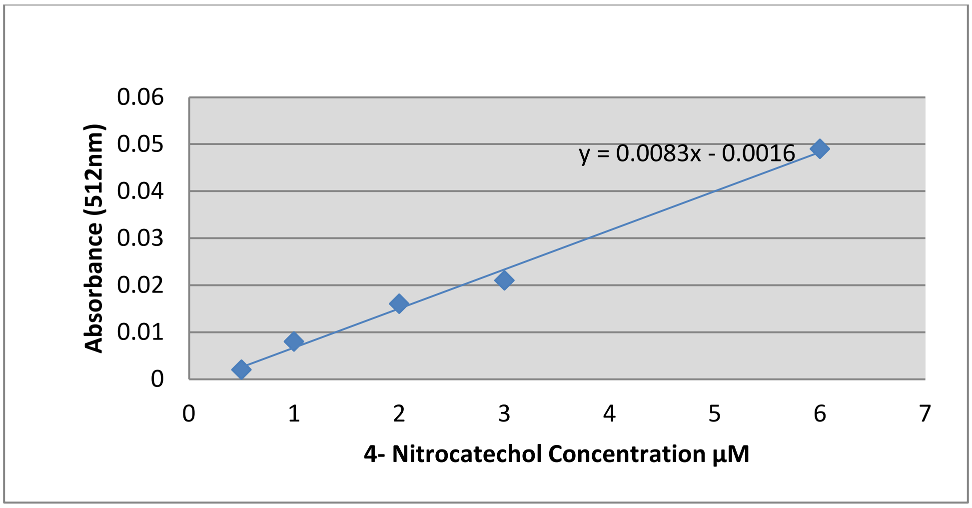


Figure (25) Calibration curve of serial dilutions of 4-nitrocatechol

The results above show that the absorbance of the hydroxylated compound (4–nitrocatechol) observed at 512 nm increases with an increasing initial concentration of the starting 4-nitrophenol, which indicates a positive relationship between concentration and absorbance. The rate of increase was almost constant (0.005 abs) for each 1 µM of 4-nitrophenol.

### 4-Nitrophenol 40 kHz Bath

The figure and the table below show the data obtained from 4-nitrophenol dosimety using a 40 kHz Bath.

Table (13) Change in absorbance of 4-nitrocatechol using a 40 kHz bath

| Time (min) | Absorbance of 4 - nitrocatechol (512nm) | Concentration of 4-nitrocatechol (µM) |
|---|---|---|
| 0 | 0 | 0.192771084 |
| 15 | 0.001 | 0.313253012 |
| 30 | 0.002 | 0.43373494 |
| 45 | 0.003 | 0.554216867 |
| 60 | 0.006 | 0.915662651 |

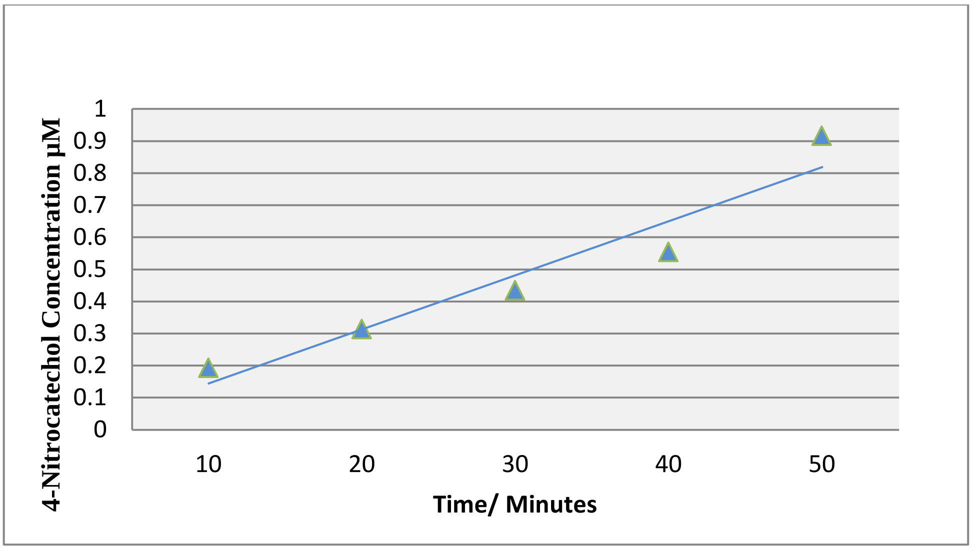


Figure (26) 4-nitrocatechol concentration versus time/minutes at 40 kHz

The higher concentration of hydroxylated compound was achieved at longer sonication time. More sonication time means that more cavitations are produced, which generate more free radicals and these can involve the subsequent oxidation reactions (Mason 2002).

### 4-Nitrophenol 850 kHz Bath

The figure and the table below show the data obtained from 4-nitrophenol dosimety using a 850 kHz Bath.

Table (14) Change in absorbance of 4-nitrocatechol over sixty minutes at 850 kHz

| Time (minutes) | 4-nitrocatechol absorbance at (512nm) | 4-nitrocatechol Concentration (µM) |
|---|---|---|
| 0 | 0 | 0.192771084 |
| 15 | 0.011 | 1.518072289 |
| 30 | 0.016 | 2.120481928 |
| 45 | 0.021 | 2.722891566 |
| 60 | 0.022 | 2.843373494 |

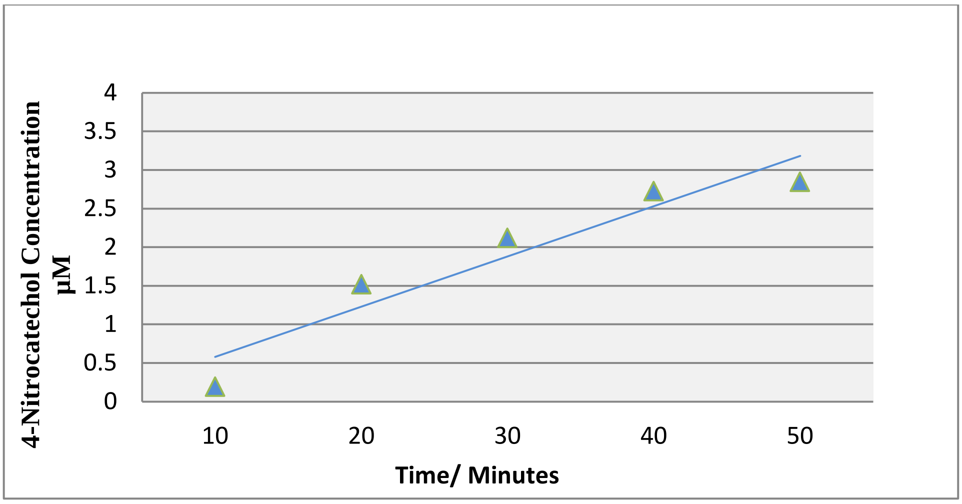


Figure (27) 4-Nitrocatechol concentration versus time at 40 kHz

The results that were achieved by using the 850 kHz bath show that the absorbance (512nm) of 4-nitrocatechol increases over time. The higher concentration of hydroxylated compound was achieved when a longer sonication time was applied. More sonication time means that more cavitations are produced, which generate more free radicals and these can be involved in the subsequent oxidation reactions and yield the hydroxlated compound (Mason 2002). A higher concentration of hydroxylated compound was achieved with 850 kHz, when compared to 40 kHz, which is attributed to increases of cavitation intensity and shorter lifespans of the cavitation bubbles at higher frequencies producing more free radicals. P-nitrophenol dosimetry is more selective than the iodide method because the oxidative reagent of p-Nitrophenol is more specific to hydroxyl radical itself. Thus more hydroxyl radicals are produced at 850 kHz.

### 3.1.2.3 Methyl Orange Dosimetry

The objective of this experiment was to characterize power ultrasound action on methyl orange in order to use it in to determine the presence of radicals formed by sonication. The initial concentration of methyl orange was 10 µmol/L. Samples were measured at 464nm in order to determine the methyl orange concentration. A standard calibration curve was plotted by measuring the series of dilutions of 10 µmol/L Methyl orange solution in RO water and analyzing at 464 nm.

Table (15) Concentration of methyl orange measured at a wavelength of 464nm

| Concentration of Methyl Orange (µM) | Absorbance (464nm) |
|---|---|
| 0 | 0.000 |
| 2 | 0.055 |
| 4 | 0.108 |
| 6 | 0.151 |
| 8 | 0.220 |
| 10 | 0.284 |

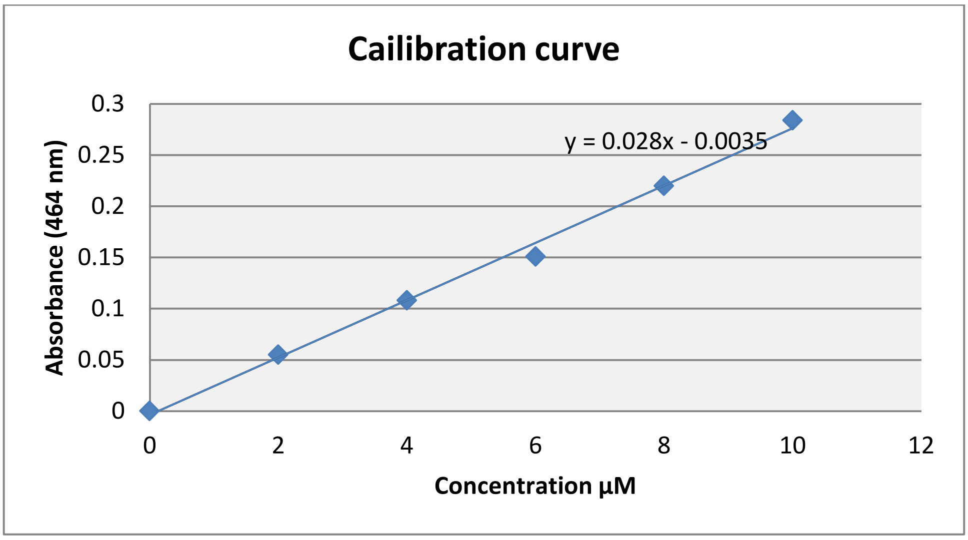


Figure (28) Calibration curve of serial dilutions of methyl orange

The results above show the calibration of methyl orange and that the absorbance (464nm) increases with increasing concentration of the substance, which indicates a positive relationship between concentrations.

$$Concentration\ of\ methyl\ orange = (x + 0.0035)/0.0280$$

$x$ represents the absorbance of Methyl orange at a specific time period. The value's 0.0280 and 0.0035 represents the gradient of the graph and is used to calculate the concentration from the absorbance. Consequently, the value of the concentration of methyl orange was determined by this equation.

40 kHz Bath

The figure and table below show the data obtained from methyl orange dosimety using a 40 kHz bath.

Table (16) Change in the absorbance and concentration of methyl orange over 60 minutes at 40 kHz

| Time (minutes) | Absorbance (464nm) | Concentration of methyl orange (µM) |
|---|---|---|
| 0 | 0.303 | 10.94 |
| 15 | 0.282 | 10.19 |
| 30 | 0.274 | 9.91 |
| 45 | 0.271 | 9.80 |
| 60 | 0.254 | 9.19 |

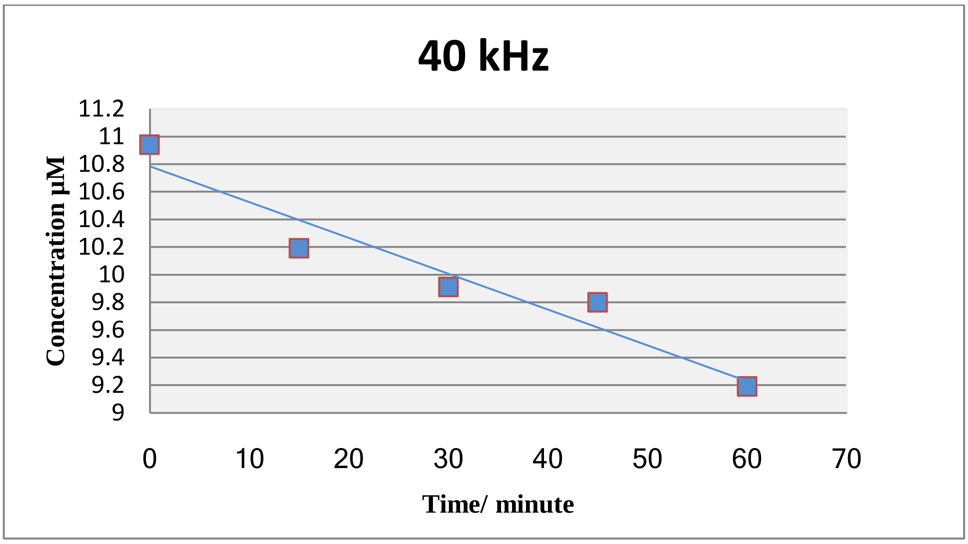


Figure (29) Rate of methyl orange decolourisation over the course of time at 40 kHz

The results have shown that the absorbance of methyl orange at 464nm decreases with an increase in sonication time. This indicates that ultrasound is able to decolourise methyl orange at 40 kHz.

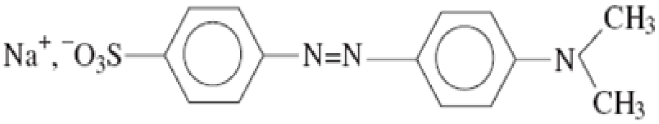


Figure (30) Methyl orange structure

The loss in colour by sonication is due to the amount of $OH^{\cdot}$ radicals produced, therefore with more $OH^{\cdot}$ radicals produced the more colour is lost. The decolourisation occurs due to the breakdown of the methyl orange (N=N bond) due to reaction with the $OH^{\cdot}$ Radicals formed (He, Grieser and Ashokkumar 2011) and a reduction in the conjugation of the coloured molecule.

850 kHz Bath

The table and the figure below show the data obtained from methyl orange dosimeter using an 850 kHz bath.

Table (17) Change in the absorbance and concentration of methyl orange over 60 minutes at 850 kHz

| Time (min) | Absorbance (464 nm) | Concentration of methyl orange (µM) |
|---|---|---|
| 0 | 0.282 | 10.16 |
| 15 | 0.246 | 8.91 |
| 30 | 0.218 | 7.91 |
| 45 | 0.200 | 7.26 |
| 60 | 0.186 | 6.76 |

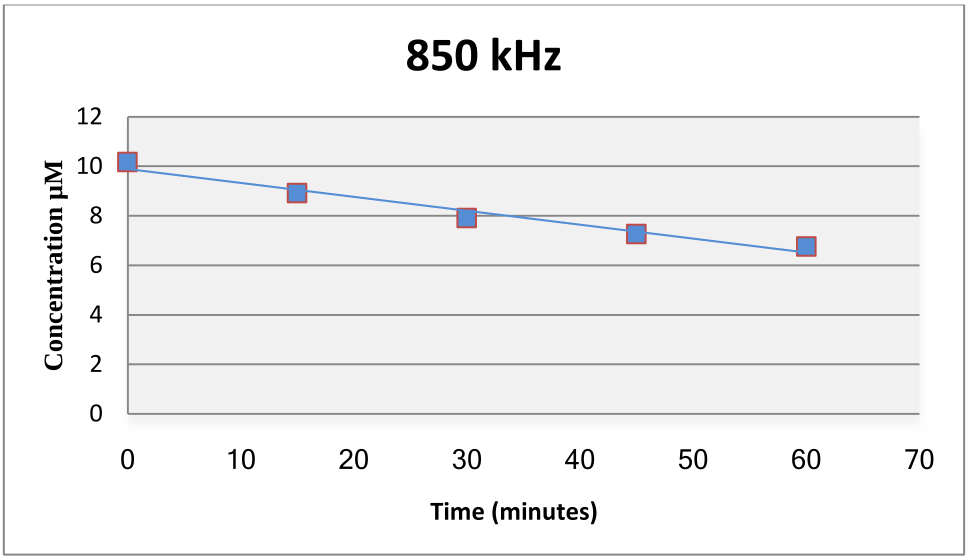


Figure (31) Rate of methyl orange decolourisation over the course of time at 850 kHz

As indicated from the results above more methyl orange is decolourised at higher frequencies (850 kHz compared to 40 kHz), which means that higher concentrations of radicals were produced. As the frequency increases the collapse of the bubble occurs more rapidly and more radicals escape from the bubbles (Mason and Peters 2002). Consequently the best frequency for radical formation again appears to be 850 kHz.

## 3.2 Electroless copper plating rate

### 3.2.1 The Conventional electroless copper plating process

Electroless copper plating is mostly used as a process for the metallization of non conductive substrates. It is used throughout the manufacturing process for the production of electronic devices and photovoltaics. Electroless processes are characterised as being high temperature processes since this has been found to be the main factor in achieving acceptable plating rates. Electroless copper plating is usually carried out between 30-70$^{o}$C. Nevertheless to reduce the energy consumption used during manufacturing lower process temperatures need to be investigated in order to reduce the cost of the manufacturing process (Cobley *et al* 2012). The tables and figures below discuss the results which were achieved with different operating temperatures.

The weight gain of the substrate is an essential method to determine the amount of the copper that is coated onto the substrate surface and is used to calculate the plating rate.  The weight of each epoxy Tg resin sample was recorded before the electroless copper plating was applied and also after the sonication treatment.  This technique can introduce knowledge about the efficiency of the treatment, as the more weight gained refers to a higher rate electroless copper plating process. The weight gained for each sample was recorded three times after processing and the average value was obtained. See section (2.10.1)

The table and figure below show the results achieved for the effect of temperature on the weight gain for epoxy samples and therefore on copper plating rate with silent conditions (No Ultrasound). The electroless copper plating rate values in this section might be considered as being a normal result for the traditional electroless copper plating process. Error bars shown are based on the standard deviations of n= 3 experiments.

Table (18) Electroless copper plating rate - silent condition

| Temperature $^oC$ | Average Copper Plating rate µm/ 25 minutes |
|---|---|
| 25 | 0.75 |
| 30 | 1.18 |
| 35 | 1.38 |
| 40 | 1.83 |
| 45 | 2.31 |
| 50 | 3.04 |

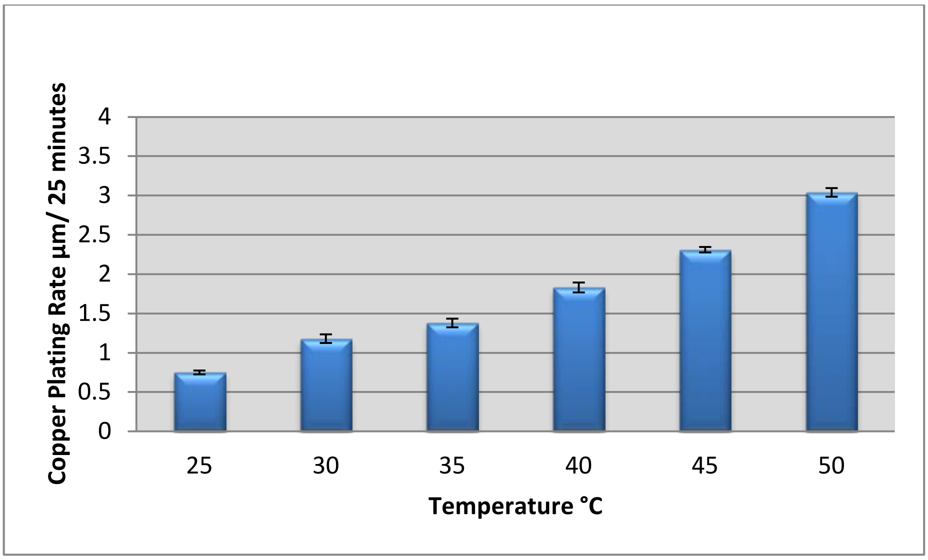


Figure (32) Electroless copper plating rate - silent condition

The highest weight gain for the epoxy sample was achieved at the highest temperature (50 $^oC$) and the copper plating rate also increased with an increase in the temperature. It is obvious that temperature has a great effect on the copper plating process as a copper plating rate of nearly 3.04 µm/25 minutes was obtained at 50 $^oC$, which is higher than other plating rates.

The effect of electroless bath temperature had been investigated by Tian and Guo (2010) in China. Their work showed that the electroless copper rate increased with an increase in the electroless bath temperature and the plating rate was decreased at lower temperatures (20, 30 $^oC$). In their work the highest plating rate was achieved at

60 $^{o}$C (Tian and Guo 2010). In 2003, work carried out by F. Touyeras showed that the electroless copper plating rate is (2.5 µm h$^{-1}$) at 46 $^{o}$C, which is lower than the plating rate value we obtained at 45 $^{o}$C (2.31 µm/ 25 minutes). The high temperature causes more energy in the chemical solution which makes the molecular solution move faster and increases mass transport; however the high electroless bath temperature would also cause a rapid oxidation process on the substrate surface which causes more electrons to be released from the anodic to the cathodic area on the substrate surface, which leads to a higher copper coverage. Also from the Nernst Frick equation an increase in the temperature will reduce the Nernst diffusion layer thickness increasing the limiting current density.

### 3.2.2 Effect of ultrasound on electroless plating rate

The effect of ultrasound on electroless copper plating has been widely investigated by researchers who tended to use higher frequency ultrasound (530 kHz) at a range of applied powers (5, 10 and 15 W) using an epoxy resin substrate (Touyeras *et al* 2001, 2003, 2005) and (Kobayashi, Chiba and Minami 2000). These studies on ultrasound utilization with electroless plating processes have shown that it can increase the plating rate. However, all these studies have investigated ultrasound with electroless copper plating at traditional operating temperatures and have not determined if ultrasound can enable an effective low temperature process (Cobley *et al.*2011).

Ultrasound and the cavitation phenomenon are known to induce microjetting in an electroless solution and this can effect the copper plating rate by thinning of the diffusion layer and enhancing the plating reaction (Ruo, Yiyun and Ciguang 1997) and (Malik and Ray 2009). It has been shown that sonication causes intense agitation and reduces the thickness of the diffusion layer at the substrate surface, which enhances the plating rate and the coverage process which gives good conductivity to the substrate surface (Ohsaka *et al.* 2008).

Ultrasound could also improve the oxidation reaction by increasing mass transport in the solution by increasing copper ion movement (Marken and Compton 1996). Electroless copper plating with high frequencies (300, 500 and 850 kHz) was also studied by (Touyeras 2005) who investigated the effect of ultrasound on both an electroless copper solution and also on colloidal palladium-tin baths. The effect of high frequency on electroless copper plating had indicated enhanced mass transfer; the high frequencies produced more bubble collapses which could enhance the copper plating rate by enhancing the oxidation process (Touyears *et a.l* 2005). These results determined that ultrasound generally affected the initial stage of the electroless copper plating process, by removing the remaining tin from the colloidal catalyst and enhancing the reduction of ionic palladium to more catalytic palladium metal.

Ultrasound is also known to be an effective method of degassing liquids. As hydrogen gas is often formed at electrodes during plating the use of ultrasound results in hydrogen degassing which could take place at the same time as copper deposition on the substrate surface. The amount of hydrogen occluded in the coating operation leads to porosity and tensile internal stress which is unwanted in the final coated products. Finally ultrasound also provides enhanced corrosion resistance of copper coatings because sonication causes a finer grain structure which leads to a good surface coverage with metal (Lu 2009).

This section will show and discuss the results which were obtained from using a 40 kHz and 850 kHz ultrasonic bath at different operating temperatures of the electroless copper process.

The table and figure below show the results achieved for the effect of ultrasound 40 kHz and 850 kHz on electroless copper plating rate. Results under ultrasonic treatment compared to the silent conditions are presented as follows. Error bars shown are based on the standard deviations of n= 3 experiments.

Table (19) Electroless copper plating rates

| Temperature$^{o}$C | Copper Plating Rate Silent µm/25 minutes | Copper Plating Rate 40 kHz µm/25 minutes | Copper Plating Rate 850 kHz µm/25 minutes |
|---|---|---|---|
| 25 | 0.75 | 0.27 | 0.64 |
| 30 | 1.18 | 1.11 | 0.91 |
| 35 | 1.38 | 1.43 | 1.4 |
| 40 | 1.83 | 1.86 | 1.79 |
| 45 | 2.31 | 2.65 | 2.71 |
| 50 | 3.04 | 3.35 | 2.94 |

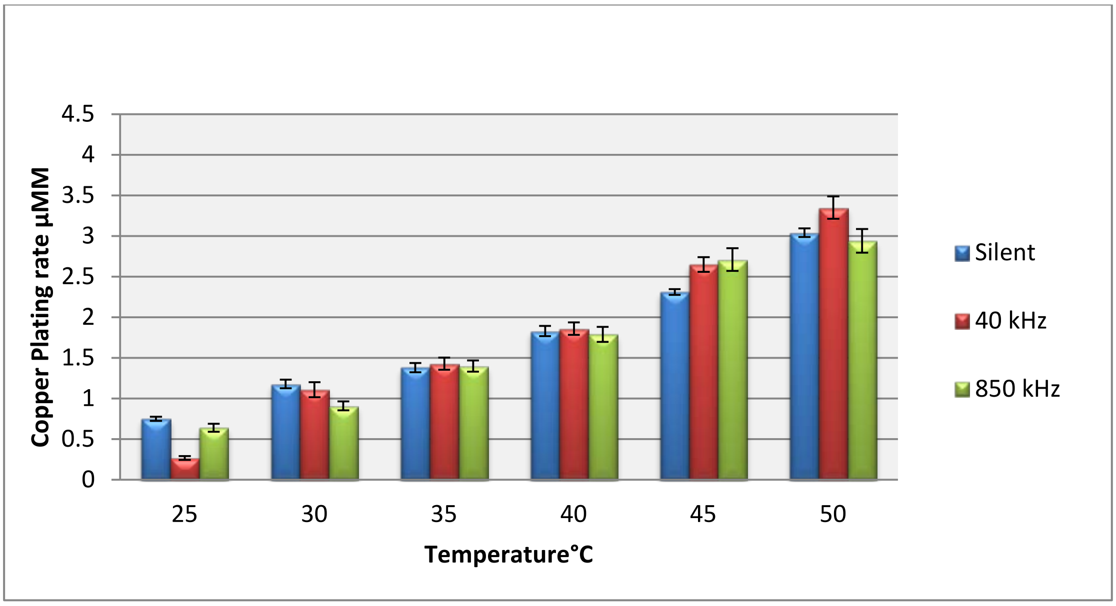


Figure (33) Electroless copper plating rate µm/ 25 minutes silent, 40 kHz and 850 kHz

The results of plating rate tests indicate that ultrasound had a little positive effect on the plating rate above 45 ºC but at low temperatures such as (25 and 30 ºC) the plating rates were either similar or slightly lower.

In order to initiate the plating process the epoxy samples used in these experiments were treated with Pd/Sn catalyst. It was thought that on application of sonication the formation of microjets would occur. These microjets could hit the substrate surface and possibly remove the catalyst species thus resulting in a poor oxidation process leading to a low plating rate. As a result the catalyst would take longer to be covered by copper metal ions at lower temperatures which would explain the lower ultrasonic copper plating rates below 35 ºC, when compared to those under normal silent conditions. The ultrasonic electroless plating rate was also investigated by Mallik and Ray in 2009, in which they obtained a higher copper deposition rate with a higher temperature used (0.15 µm at 25 °C) (0.10 µm at 19 °C). The plating rate was higher with ultrasound because of the enhanced mass transport introduced by using ultrasound which resulted in a higher concentration of copper on the substrate surface (Mallik and Ray 2009). The increases in plating rate above 45 $^{o}$C by influence of ultrasound could be attributed to the increase in heat and mechanical agitation which comes from the cavitation effect (Hu *et al.* 2011).

### 3.3 X-ray photoelectron spectroscopy (XPS) Analysis of Substrate

All previous plating experiments which utilised ultrasound have shown that a low plating rate is achieved at low temperatures (25 and 30 $^{o}$C). It was thought that ultrasound induced microjetting may lead to catalyst removal resulting in a poor oxidation process on the substrate surface. In addition, at low temperatures the catalyst on the substrate surface might be taking a longer time to be covered by metallic copper than at high temperatures thus leaving it exposed to the ultrasound microjets for a longer time.

In this experiment 4 coupons were processed using different conditions see section (2.10.5). These were sent for XPS analysis at Loughborough Surface Analysis Limited (LSA Ltd). The solutions (1 to 3) used in these experiments can be found in Section (2.5.1).

These experiments were designed to show whether Pd was removed from the substrate surface when ultrasound was applied. Solution 3 (see section 2.5.1) was used for these experiments but in the absence of copper. This was to avoid the epoxy test coupons plating with copper which would have masked the underlying Pd during XPS analysis.

The table and figure below show the effect of ultrasonic irradiation on Pd concentration measured on the epoxy substrate.

Table (20) - Pd concentration measured at the substrate surface.

| Field | Pd Atomic concentration % |
|---|---|
| 4 minutes Silent | 4.8 |
| 4 minutes 40 kHz | 4.5 |
| 10 minutes Silent | 2.9 |
| 10 minutes 40 kHz | 0.1 |

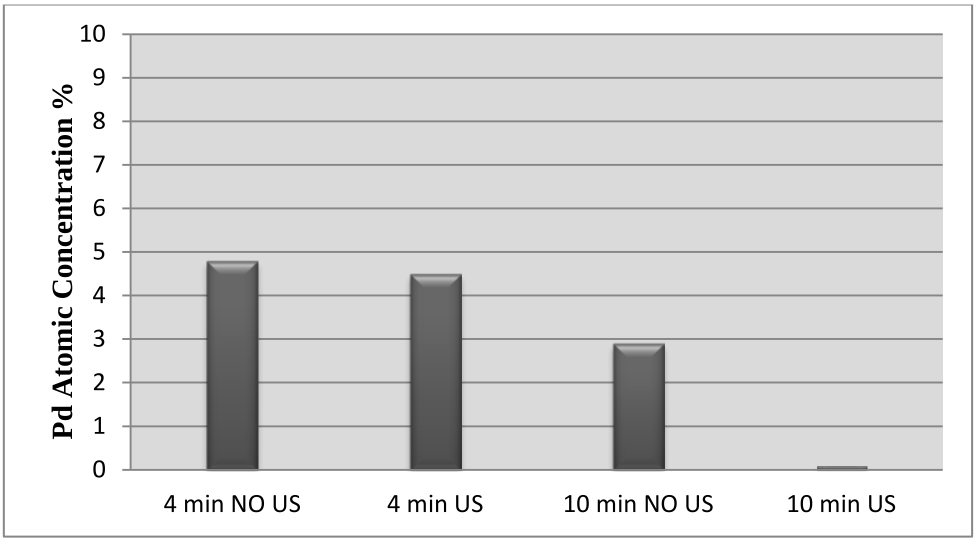


Figure (35) Effect of ultrasonic irradiation on Pd concentration measured at the substrate surface.

The relative concentrations of Pd on the epoxy samples obtained at four minutes under silent conditions and with 4 minutes sonication are similar; therefore the four minutes of sonication time has little effect on the Pd concentration. After 10 minutes the picture is more dramatic. Ten minutes of sonication appears to remove most of the Pd from the surface of the epoxy with only 0.1% Pd remaining, while silent conditions still retain 2.9% of Pd.

It seems likely that the catalyst needs enough time to be coated with copper before the ultrasound is turn on. This protects it from being removed from the substrate surface by microjetting and cavitation. This could be the reason behind the negative effect of ultrasound at low temperatures see section (3.2.2), where the plating rate is slow and the catalyst is exposed to ultrasonic irradiation for the longest time before being coated by copper. Higher temperatures (above 35$^{o}$C) provide a faster rate of coverage and so protect the Pd catalyst from removal. Therefore in order to allow coverage of the Pd the plating must either occur at higher temperatures (unwanted in this case) or there must be a delay introduced prior to sonication in order to allow coverage of the Pd before sonication and microjets are introduced into the plating bath.

### 3.4 Delays in Sonication

By the delaying the time before ultrasound is turn on it was hoped that this would allow time for the Pd colloid to being covered with copper and thus would prevent it from being removed from the substrate surface by ultrasonic microjetting. Figure 36 shows the effect of introducing a sonication delay time on the copper plating rate. All previous results which were achieved with sonication have shown a poor plating rate at low temperatures see section (3.2.2, 3.2.3 and 3.3).

All experiments were conducted by using the same steps as sections (2.6, 2.7 and 2.8) with 40 kHz and 850 kHz however introducing a 7 minutes delay time before the ultrasound was turned on (see section 2.9)

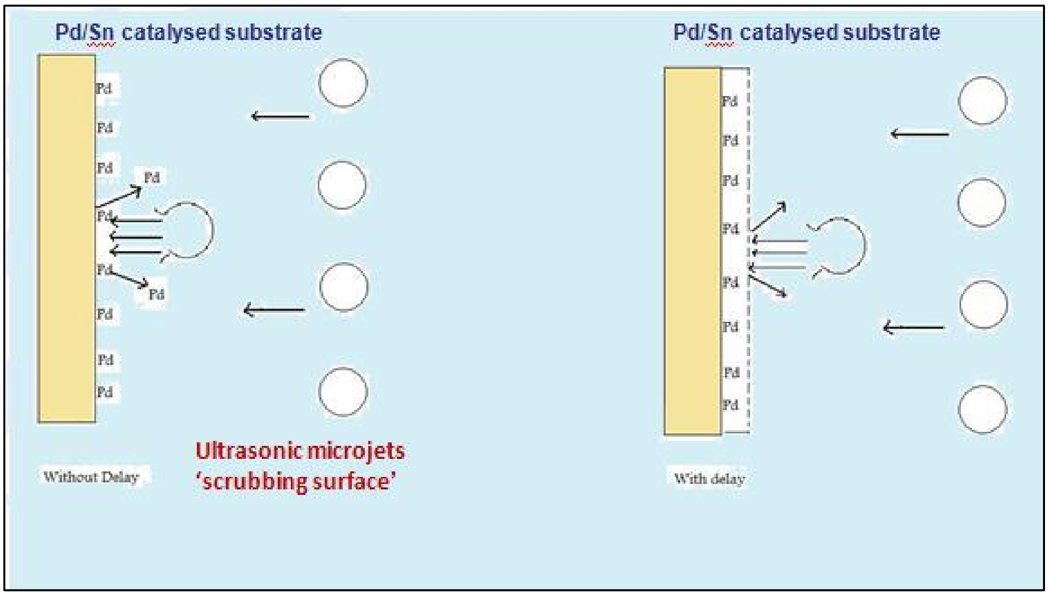


Figure (36) Delay time effects on Pd/Sn concentration on the substrate surface.

The poor plating results at low temperatures have supported the theory that the acoustic cavitation could be more aggressive at low temperatures and the catalyst on the substrate surface would take longer to be covered by copper at low temperatures, this would also explain the results below 35 ºC.

The table and graph below show the results achieved for the effect of different delay times on the electroless copper plating rate. Results of 40 kHz ultrasound and at 40 $^{o}$C with (2, 4, 7 and 10 minutes delay) and compared to 0 time delay are presented as follows:

Table (21) Effect of 40 kHz sonication on electroless copper plating with various delay times

| Delay Time (Minutes) | Copper Plating Rate 40 kHz (40 $^{o}$C) µm/ 25 minutes |
|---|---|
| 0 | 1.54 |
| 2 | 1.43 |
| 4 | 1.95 |
| 7 | 2.54 |
| 10 | 1.96 |

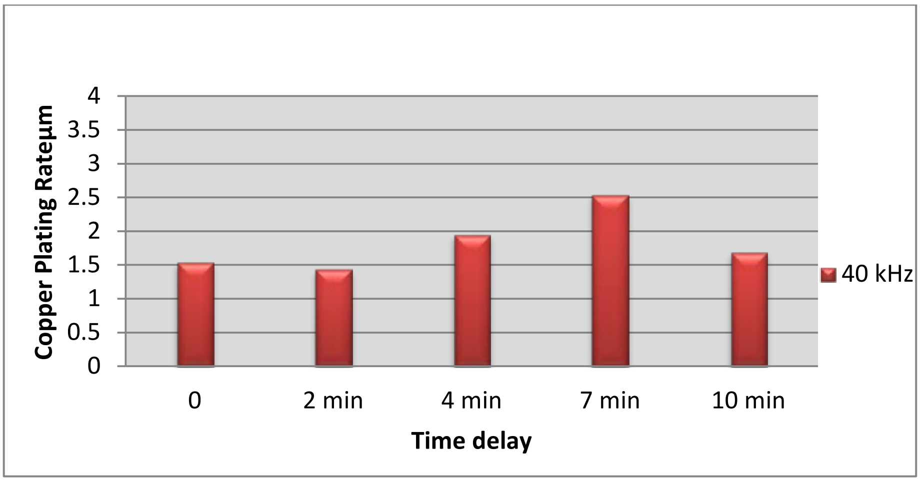


Figure (37) Effect of delay times on electroless copper plating (40 kHz)

The results show that a 2 minute delay, compared to no delay time, had very little effect on the electroless copper plating rate under ultrasonic irradiation. This indicates that 2 minutes delay is not enough for the catalyst to be covered by copper. As the delay time is increased to 4 minutes, then 7 minutes, the plating rate increases. The results indicate that the best time for the catalyst to be covered by copper is 7 minutes delay before allowing the ultrasound to be turn on. As the delay time is increased above 7 minutes to 10 minutes the plating rate decreased again. A 10 minute delay is enough time for the Pd catalyst to be covered by copper however the plating rate is low simply because these experiments were performed in the absence of any agitation (as ultrasound is also a source for agitation). Reducing agitation for 10 minutes at the start of the plating process reduces mass transport of ions towards the substrate surface and as a result the overall plating rate falls. The 15 minutes of remaining agitation (10 minutes of no sonication followed by 15 minutes sonication for a 25 minute total treatment time) might be not enough to achieve the positive effect of ultrasound in electroless copper plating.

### 3.4.1 Effect of 7 minutes delay on electroless plating rate

As XPS results have shown a delay time is required in order to have effective plating rate enhancement when using ultrasound and sonication. The optimum delay was shown to be 7 minutes.

The table and figure below show the results achieved for the effect of 40 kHz and 850 kHz ultrasound on the electroless copper plating rate with 7 minutes delay. The whole treatment time was 25 minutes (7 minutes silent i.e. no agitation) and (18 minutes sonication) at different operating temperatures. Results are presented as follows. Error bars shown are based on the standard deviations of n= 3 experiments.

Table (22) Effect of 7 minutes delay on electroless plating rate

| Temperature $^{o}$C | Copper Plating Rate 40 kHz µm/25 minutes | Copper Plating Rate 40 kHz Delay 7 minutes µm/25 minutes | Copper Plating Rate 850 kHz µm/25 min | Copper Plating Rate 850 kHz Delay 7 minutes µm/25 min |
|---|---|---|---|---|
| 25 | 0.27 | 0.31 | 0.64 | 0.67 |
| 30 | 1.11 | 1.19 | 0.91 | 1.22 |
| 35 | 1.43 | 1.65 | 1.4 | 1.43 |
| 40 | 1.86 | 2.54 | 1.79 | 2.05 |
| 45 | 2.65 | 2.72 | 2.71 | 3.05 |
| 50 | 3.35 | 3.86 | 2.94 | 2.8 |

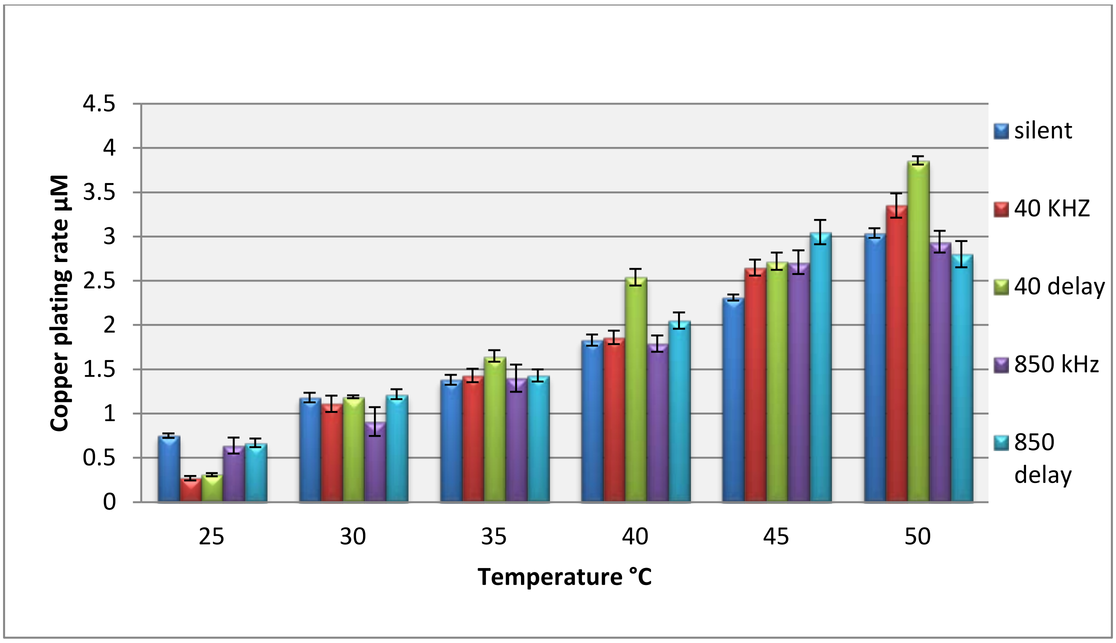


Figure (38) Electroless copper plating rate under different conditions

As can be seen from the results in Figure 38 the plating rate increases with a temperature increase of the plating bath which is as expected. The highest plating rates are achieved with a bath temperature 50 °C. However what is also of note is that the highest plating rates at several temperatures are the ones achieved when a delay of 7 minutes is introduced to the plating bath when employing 40 kHz sonication. The most noticeable value was obtained at 40 ºC with a delay of 7 minutes, which was almost the same as the value obtained for the plating rate at 45 ºC.

850 kHz does not appear to be as effective as 40 kHz however introducing a 7 minute delay to this process is also of benefit, however not to the degree as the 40 kHz process. The 850 kHz frequency produces cavitation bubbles smaller than the bubbles which are formed at low frequencies which results in less effective mixing and mass transport of materials leading to a lower plating rate (Malik and Ray 2009).

### 3.5 Effect of air bubbling on electroless copper plating

Most electronic industries have an aim to improve the copper plating rate, particularly when electroless copper baths are used, as this might introduce a good substrate surface in terms of thicker deposition. A high plating rate could also provide more reliability of the deposit and stabilizers are normally added to the electroless bath in order to stop the formation of undesired cuprous oxide particles which can also affect the deposit. One of the ways to improve plating rate is to employ air bubbling in order to agitate the electrolyte. Air bubbling has also been shown to increase the stability of the bath by up to 20 times in contrast to a bath without air bubbling. This is due to the additional air being able to oxidize any copper species formed, and thus avoiding bath decomposition via copper disproportionation (Hanna, Hamid and Aal 2003).

### 3.5.1 The electroless copper plating process with air bubbling agitation

Figure 39 and table 23 below show the results achieved for the effect of air bubbling agitation on the electroless copper plating rate.

Table (23) Effect of air bubbling on electroless plating rate

| Temperature $^{o}$C | Copper Plating Rate Silent | Copper Plating Rate Silent + air | Copper Plating Rate 40 kHz delay | Copper Plating Rate 40 + air | Copper Plating Rate 850 kHzdelay | Copper Plating Rate 850 + air |
|---|---|---|---|---|---|---|
| 25 | 0.75 | 0.53 | 0.31 | 0.34 | 0.67 | 0.72 |
| 30 | 1.18 | 0.65 | 1.19 | 0.61 | 1.22 | 1.22 |
| 35 | 1.38 | 1.37 | 1.65 | 1.11 | 1.43 | 1.28 |
| 40 | 1.83 | 1.57 | 2.54 | 1.85 | 2.05 | 1.65 |
| 45 | 2.31 | 2.16 | 2.72 | 2.61 | 3.05 | 2.89 |
| 50 | 3.04 | 3.31 | 3.86 | 3.42 | 2.8 | 1.78 |

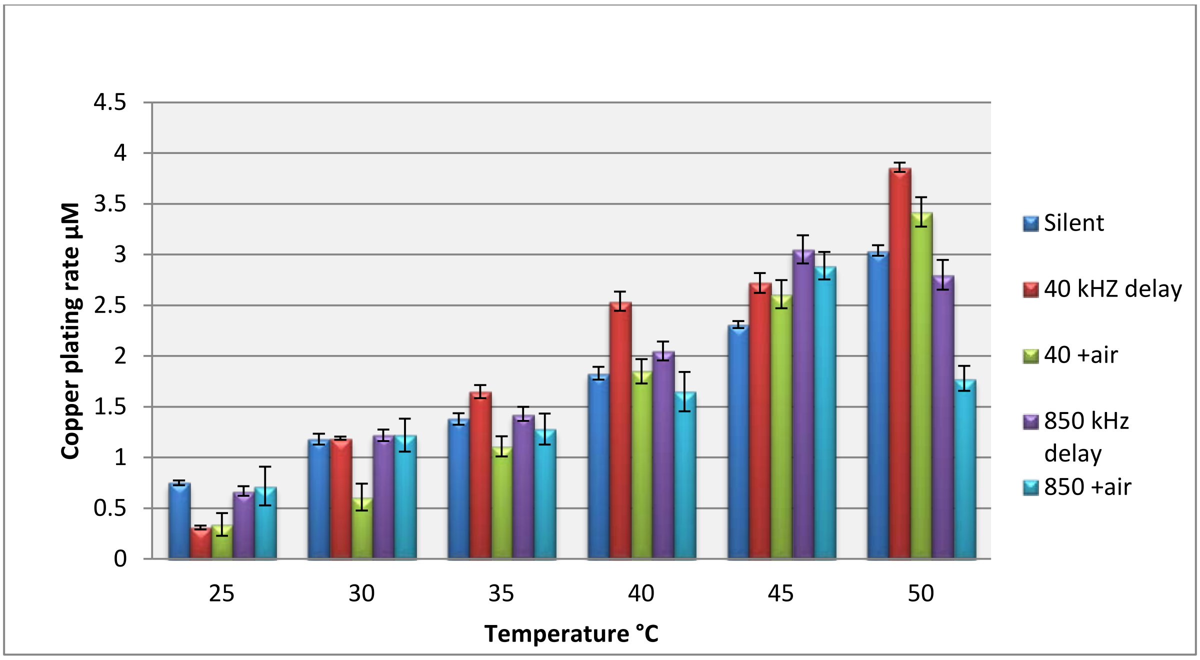


Figure (39) Electroless copper plating rate silent, 40 kHz and 850 kHz condition, versus air bubbling

From the figure above, the electroless copper plating rates produced during air bubbled experiments were lower than the values obtained with no additional air. These results are considered as non desirable as one of the aims of this project was to achieve high plating rates at lower temperatures. The use of air bubbling leads to a longer bath life because the air oxidises any copper species formed thus avoiding bath decomposition via copper disproportionation. The presence of air also appears to reduce any destabilising effect on the EDTA present in the copper bath thus again leading to stabilisation of the bath. However in the experiments performed the introduction of air agitation, alongside the use of ultrasound, had a negative effect on plating with 40 kHz and delay 7 minutes and also on plating with 850 kHz and delay 7 minutes.

The figure above shows that using air bubbling caused a significant drop in plating rate at all temperatures (25- 50 $^{o}$C). Air agitation reduces the positive effect of ultrasound since some cavitation energy would be lost in attempting to degas the electroless copper solution. The increasing level of vapour in the electroless copper solution can interfere with sonication by making the cavitational collapse less effective, as a result negating the positive influence of using ultrasound. Touyeras also confirmed that the ultrasonic effects are influenced by the hydrogen degassing process that occurs when air bubbling is applied. The conventional electroless copper plating process uses formaldehyde as a reducing agent and it has been found that 1 mol of hydrogen gas is generated for each 1 mol of copper deposited (Sone *et al.* 2004). This effect is very harmful for the metal coating because hydrogen degassing takes place at the same time as metal deposition (Touyeras *et a.l* 2001). Therefore if the degassing process is the preferential route for ultrasound the deposition rate is therefore reduced. Air bubbling is therefore not of benefit to an ultrasonic electroplating process.

### 3.6 Effect of using glyoxylic acid as a reducing agent on plating rate

Electroless copper plating is used to provide a conductive layer coating on a nonconductive surface (Cheng 1997). The most common industrially used electroless copper plating solution contains formaldehyde as the reducing agent and is normally operated between 40 and 60 $^{o}$C (Wu and Sha 2009). It is also employed due to the low cost and high plating rate achieve by using it (Anik *et al.* 2012). However, in addition to the hazardous nature of formaldehyde as a carcinogen, and the high toxicity for formaldehyde in the waste of the electroless copper solution, many hazardous gases may also be released during the operation of this bath (Anik *et al.* 2012). It is therefore important to try and identify a replacement for the formaldehyde reducing agent which is less harmful and less toxic. This less harmful substitute may be glyoxylic acid.

The electroless copper process can also plate onto an epoxy substrate by using glyoxylic acid as the reducing agent at temperatures above 45$^{o}$C (Wu and Sha 2009). Several of these processes have been investigated at the traditional plating temperatures (45$^{o}$C- 60 $^{o}$C). Lijuan Wang had performed similar experiments at a high temperature of 55 $^{o}$C but he used a wood veneer instead as the substrate. In his work the copper plating rate increased at 30 minutes (Wang, Sun and Li 2011) when using glyoxylic acid as the reducing agent, thus indicating its potential for use in the plating process.

This section shows the plating rates achieved by using glyoxylic acid ($C_2H_2O_3$) as the reducing agent at different temperatures.

### 3.6.1 The conventional electroless copper plating process using glyoxylic acid

The conventional electroless copper plating process is used with a normal operating temperature of 46 °C. The plating process with formaldehyde as a reducing agent can be described in the following reaction:

$$Cu^{+2} + 2HCHO + 4OH^{-} \longrightarrow Cu + H_2\uparrow + 2H_2O + 2HCO_2^{-}$$

The plating process with glyoxylic acid as the reducing agent is similar but a different reaction as follows:

$$Cu^{+2} + 2CHOCOO^{-} + 4OH^{-} \longrightarrow Cu + H_2\uparrow + 2H_2O + 2C_2O_4^{-}$$

In these two reactions, with plenty of hydroxyl ions, the copper ion is reduced into copper atom and the formaldehyde, or glyoxylic acid, is oxidized into a certain kind of acid (for formaldehyde it is formic acid and it is oxalic acid for glyoxylic acid). Several researchers have reported successful electroless copper plating at 45 °C in both formaldehyde and glyoxylic acid solutions (Wang, Sun and Li 2011).

The table and figure below show the results achieved by using glyoxylic acid as the reducing agent in the electroless copper plating process with silent conditions at different temperatures. Results when using glyoxylic acid are compared to the results when using formaldehyde and are presented as follows.

Table (24) Results of electroless plating rate using glyoxylic acid compared to formaldehyde

| Temperature °C | Silent copper plating rate µm/25 minutes glyoxylic acid | Silent copper plating rate µm/25 minutes formaldehyde |
|---|---|---|
| 25 | 0.33 | 0.75 |
| 30 | 0.44 | 1.18 |
| 35 | 0.63 | 1.38 |
| 40 | 0.81 | 1.83 |
| 45 | 0.91 | 2.31 |
| 50 | 1.25 | 3.04 |

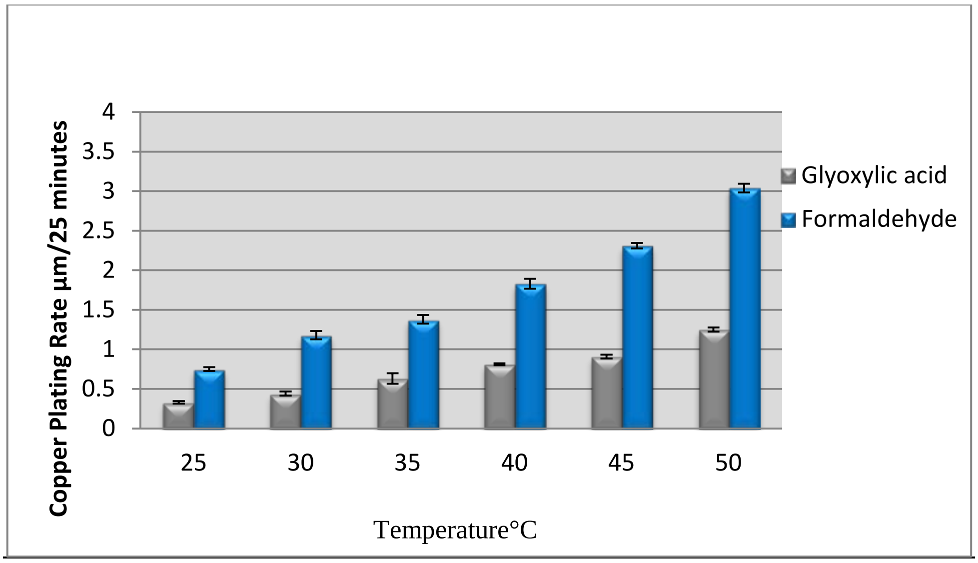


Figure (40) Results of electroless plating rate using glyoxylic acid compared to formaldehyde

As can be seen in the figure above there is a huge difference between the plating rates achieved when using formaldehyde as the reducing agent compared to glyoxylic acid. Glyoxylic acid has dropped the copper plating rate to more than half the value achieved with formaldehyde at all the temperatures used. This is due to slow oxidation of glyoxylic acid at the pH values employed. The pH value affects the oxidation process in the electroless plating reaction causing a rapid oxidation process at high pH and low oxidation process at low pH as the electroless copper plating rate increases with an increase in the pH (Anik *et al.* 2012). The main reason behind the big difference between the plating rates is that glyoxylic acid appears to react with the sodium hydroxide, which is used to keep the pH constant in the copper solution. As this reaction reduces the pH this leads to a low plating rate. Electroless copper plating rate increases with an increase of the pH from 8 - 12.5 (Anik *et al.* 2012).

The unpromising electroless copper plating results achieved by using glyoxylic acid showed that using this acid was pointless with the electroless plating process therefore there was no need to apply ultrasound as ultrasound would not improve or increase the pH value required for this electroless solution.

### 3.7 SEM Scanning Electronic Microscope

After electroless copper plating, samples from each experiment were dried in the oven for 24 hours to enable SEM analysis. Samples after treatment were tested using a Jeol

JSM-6060LV scanning electronic microscopy (SEM). Photographs for samples were taken at particular magnification (1000 and 10,000). Moreover, the texture of the substrate surface was assigned by grading each photograph from 0-10. This technique was essential in order to determine the influence of ultrasound on the actual substrate surface. The grain structure and sizes were graded as follows:-

i- Grade (0) indicates a finer grain structure (eg. smooth surface)

ii- Grade 10 indicates a larger grain structure (eg. extreme change in surface morphology).

Pictures by SEM were graded visually and the scale for assessing the pictures can be found in (2.10.2).

### 3.7.1 Effect of Ultrasound on SEM

SEM pictures were graded visually and the values obtained from silent conditions at different temperatures were compared those for ultrasound at 40 kHz and 850 kHz and exhibited in figure (41) as follows.

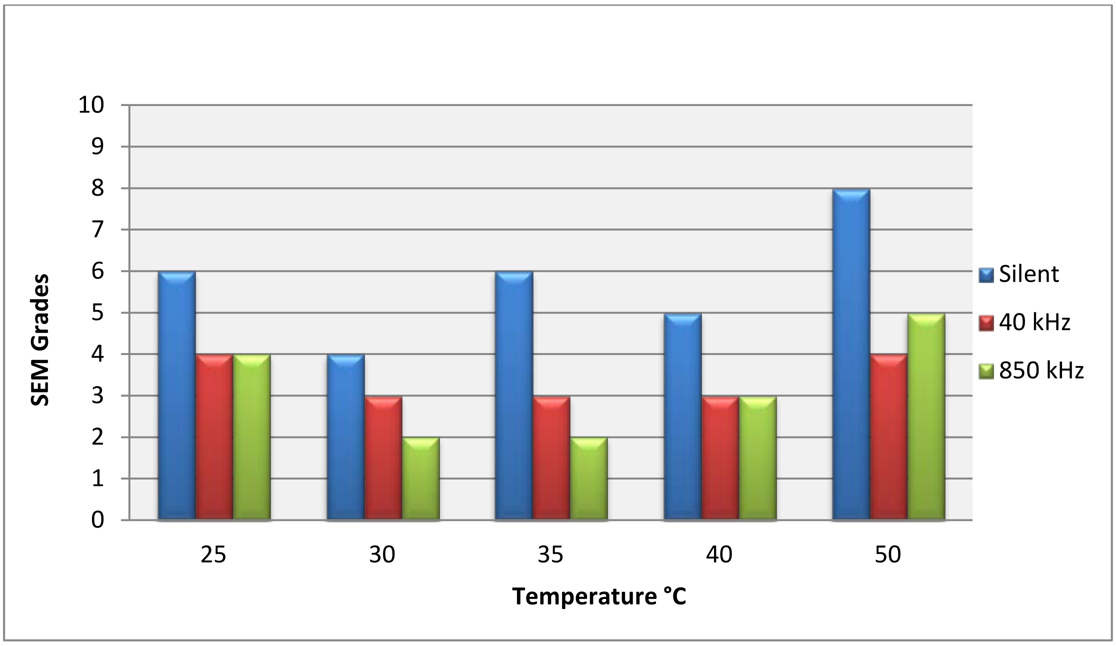


Figure (41) Effect of 40 kHz and 850 kHz sonication on SEM texture grade

The similarity of the SEM results could be considered as evidence that there is no relevance between the electroless copper plating rate and the grain structure size (Wu and Sha 2009). Therefore, the 2 point disparity in the silent SEM grade between (30 and 35 $^{o}$C) could be considered as being a tiny difference in grain structure. The significant difference is seen at 50 °C which achieved a grade of 8 indicating a double grain structure size than that obtained at 30 °C. The higher SEM grade at higher temperature could be attributed to the fact that the plating process reaction is more rapid and forms larger grain structures (Su *et al*. 2011). It is easy to see in figure (41) that finer grain structures were produced by the application of ultrasound at both 40 kHz and 850 kHz when compared to the conventional silent process. This can be attributed to the microjetting effect during the copper deposition which prevents the formation of larger grains, this results in a good surface coverage by the plated metal ions thus aiding corrosion resistance.

### 3.7.2 Effect of 7 minutes delay on SEM results

The effect of introducing a 7 minute delay on grain structure was examined at 40 kHz and 850 kHz and compared to conventional silent conditions over a range of temperatures. Again SEM pictures were graded visually. Bar charts missing in the figure below represent a grade zero which means a very fine grain structure.

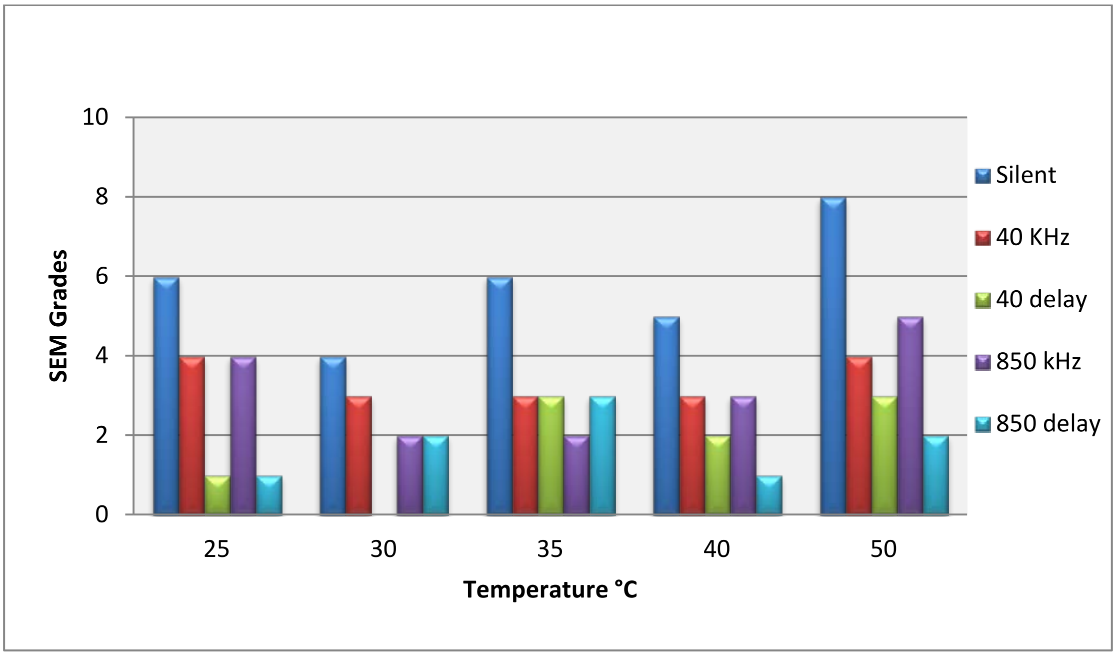


Figure (42) SEM texture grade at different temperatures with 40 kHz and 850 kHz

As can be seen in figure 42 above introducing a time delay into the sonication process results in a significant drop in grain size. This produces a finer grain size and a smoother deposit surface for all samples treated with 40 kHz and 850 kHz ultrasound.

This is very clear at the low temperatures of 25 and 30 °C. The delay in sonication time reduces surface damage which is the result of microjet sonication. Ultrasound is also capable of inducing crystal breakage which may also cause a finer grain structure size (Malik and Ray 2009). The SEM results from this section indicate that a delay time before applying ultrasound is a process with the potential to enable finer grain structure production.

### 3.7.3 Effect of air bubbling on SEM results

Pictures by SEM were graded visually. Values obtained by using air bubbling agitation on electroless copper plating rate with silent condition, 40 kHz and 850 kHz sonication are compared to the results obtained with the conventional no air experiments. All the results are exhibited in figure (43) as follows. Bar charts missing in the figure below represent a grade zero which means a finer grain structure.

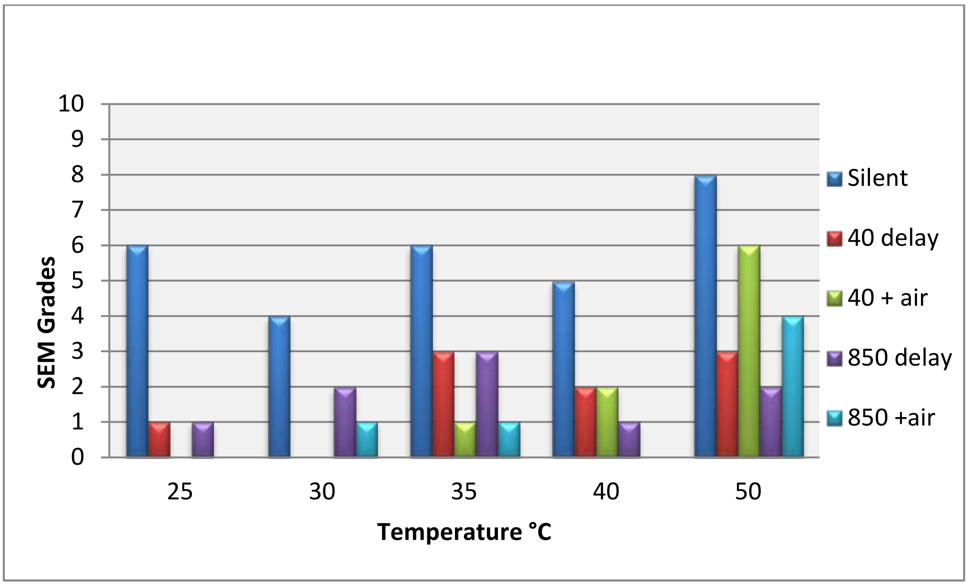


Figure (43) SEM texture grade at different temperatures under air bubbling agitation treatment compared to no air bubbling

The SEM values for the air bubbling experiments at lower temperatures were lower than those in the absence of air meaning that additional air bubbling causes a finer grain structure. A smaller grain size refers to a smoother epoxy surface The highest plating rate for the air bubbled experiments was obtained at a temperature of 50 °C and the highest SEM grade for the air bubbles experiment was also obtained at the same temperature. On the whole additional air bubbling appears to produce a smaller grain structure at temperatures below 40 C but this effect appears to be reversed at higher temperatures, when ultrasound is less effective. This may be due to the fact that ultrasound is effectively degassing the solution thus allowing smaller grains to form. At higher temperatures the degassing process may be less effective thus additional air is reflected in the deposits having a larger grain structure.

### 3.8 Gloss Meter reading

A gloss meter is a device which is used for measuring the reflected light from the substrate surface, in other words its brightness. It is also utilized to confirm the physical changes on the surface of materials after treatment, such as the smoothness of the surface. A high gloss meter reading also refers to a more finer grain structure of the metal deposit (Cobley and Saez 2011). A low gloss meter reading indicates less brightness and more roughness of the surface.

Gloss can also be a measure of the quality of a surface, for instance a drop in the gloss of the coated surface may indicate problems with it and these problems may lead to other failures such as poor adhesion or lack of protection for the coated surface. When electroless copper plating is applied a fine grained electroless copper deposit is desirable for any copper coating applications which could reflect the smoothness of the surface. It can also indicate good corrosion resistance and conductivity, necessary for electrical components such as circuit boards. This technique was previously utilized by Mkhlef (2010) and Cobley (2010) at Coventry University.

#### 3.8.1 Effect of ultrasound on gloss meter reading

In figure (44), the average gloss meter values for epoxy samples are shown as follows. The measurement was performed by taking the average of four readings for each sample and also for both faces, with a horizontal reading and vertical reading being taken. See section (2.10.3) Error bars shown are based on the standard deviations of n= 3 experiments.

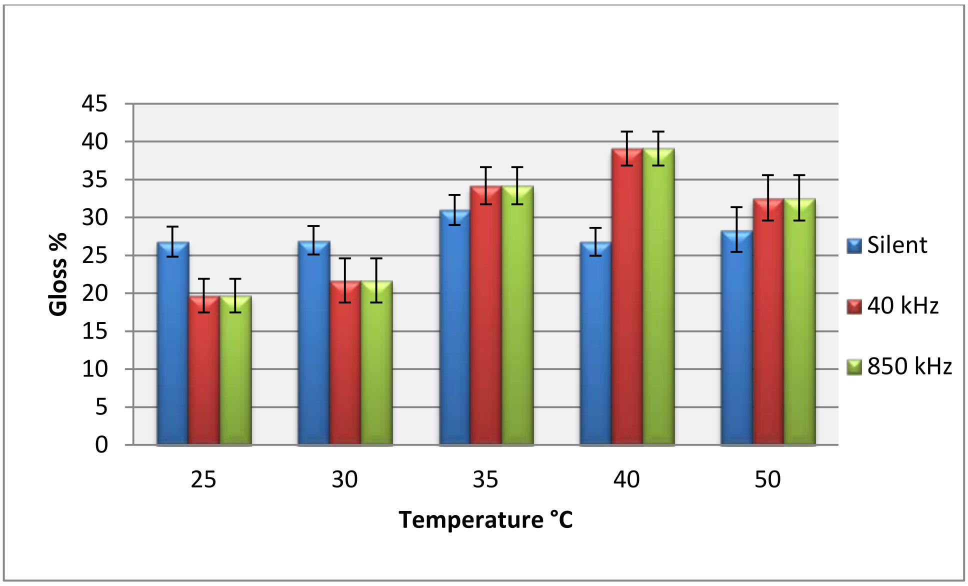


Figure (44) Effect of temperature on gloss readings after conventional copper plating

The gloss meter values show little change under all treatment conditions and all temperatures used, with a brightness ranging between 27% to 39% suggesting a similar shiny surface at all temperatures. The shiniest surface was produced at 40 $^{o}$C when using ultrasound with higher temperatures producing shinier surfaces on the whole. This could be the result of effective hydrogen degassing at 35 and 40 $^{o}$C which would influence the metal coating on the substrate surface by avoiding porosities on the surface which would produce low gloss meter readings.

### 3.8.2 Effect of 7 minutes delay on gloss meter reading

In figure (45) the effect of introducing a 7 minute delay on brightness was examined at 40 kHz and 850 kHz and compared to conventional silent conditions over a range of temperatures.

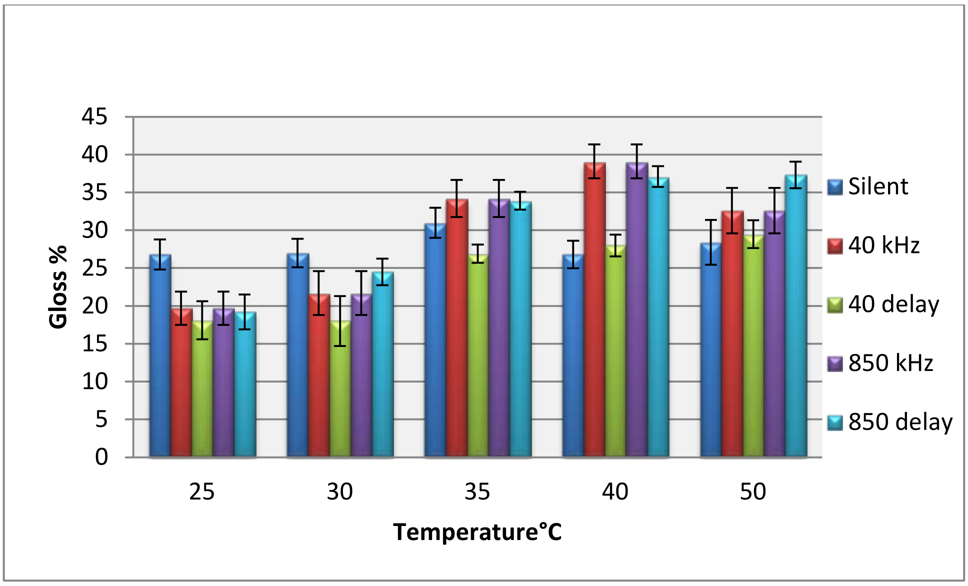


Figure (45) Effect time delay on gloss meter readings under various conditions

On the whole brightness slightly increases with a temperature increase. Ultrasound appears to benefit the process at higher temperatures with a 7 minute delay producing a lower gloss reading for both 40 and 850 kHz. The lower readings achieved for the delayed experiments may simply be due to the reduced time the solution is exposed to sonication and hence the benefits of ultrasonic degassing and microjetting resulting in a larger grain structure which could be more porous, thus giving slightly reduced brightness of the coating.

### 3.8.3 Effect of air bubbling on gloss meter results

In figure (46), gloss meter values for epoxy samples after electroless copper plating process with air bubbling agitation are measured and compared to results obtained with no air bubbling. Results are shown as follows.

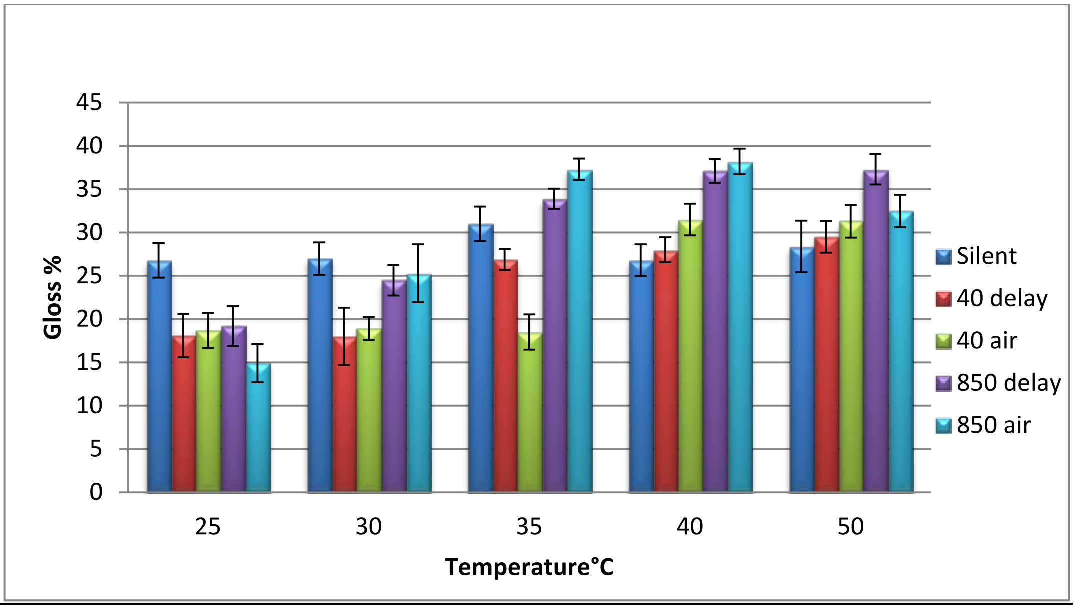


Figure (46) Gloss meter readings at different temperatures

Here again brightness increases with temperature increase for most experimental conditions with ultrasound being of more benefit at the higher temperatures. The use of air bubbling is variable. Use of additional air appears to benefit the 40 kHz process at all temperatures bar 35 °C. These results could be correlated with the SEM results obtained under the same conditions. The higher gloss meter reading means more light is reflected from the surface suggesting a smooth surface was introduced. However for 850 kHz air bubbling is detrimental at 25 and 50 °C. 850 kHz produces less effective cavitation and can therefore be expected to be less effective at degassing solutions. With cavitation already being less effective at higher temperatures this could result in more porous deposits with reduced gloss readings.

### 3.9 Adhesion Grade

Adhesion between the substrate surface and the metal coating is an essential requirement for most of the electronic and metal finishing industries (Siau 2005 and 2006). Indeed, the adhesion level for the product would actually determine the final quality of that product. In order to achieve good adhesion, an optimised metal plating needs to be applied which depends on the substrate and the metal involved in the processes. Generally, good electroless copper plating processes should be associated with good adhesion results.

### 3.9.1 Effect of ultrasound on adhesion grade

Adhesions were graded visually (see section 2.10.4) for epoxy samples after electroless copper plating. Grades for the values obtained from a silent, 40 kHz and 850 kHz condition at different temperatures are exhibited in table 25 and figure (47) as follows.

Table (25) Adhesion grade at different temperatures at silent, 40 kHz and 850 kHz

| Temp | silent | 40 kHz | 40 delay | 850 kHz | 850 delay |
|---|---|---|---|---|---|
| 25 | 9 | 7 | 6 | 6 | 6 |
| 30 | 9 | 7 | 7 | 6 | 7 |
| 35 | 9 | 8 | 8 | 8 | 9 |
| 40 | 10 | 9 | 9 | 9 | 9 |
| 50 | 8 | 9 | 10 | 10 | 9 |

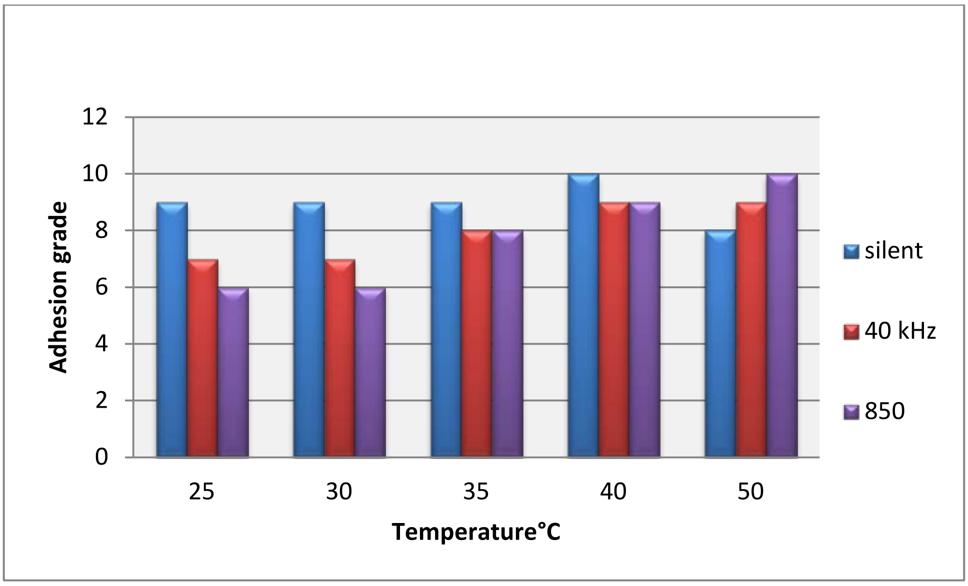


Figure (47) Adhesion grade at different temperatures at silent, 40 kHz and 850 kHz

Adhesion values for all samples increase with an increase in temperature, apart from the silent conditions experiments at 50 °C. This can be attributed to high grain deposition produced at the surface which indicates a good copper coverage with increased temperatures. The finer grain structure caused by using 40 kHz and 850 kHz introduced a lower adhesion value compared to silent conditions at temperatures below 50 °C. That difference could be caused by the ultrasound affecting hydrogen degassing which would influence the metal coating on the substrate surface. This could introduce porosities on the surface which would produce low adhesion between the metal deposit and the substrate surface. Hydrogen degassing would take place within the metal coating and would introduce a low wettability of copper solution on the epoxy surface. Therefore, the adhesion bond between the surface and the surface becomes weak and a low adhesion value is obtained (Touyeras *et al*. 2005).

### 3.9.2 Effect of 7 minutes delay on adhesion grade

Adhesions were graded visually for epoxy samples after electroless copper plating process. Grades for the values obtained from a silent, 40 kHz and 850 kHz conditions with and without delay time at different temperatures and are exhibited in figure (48) as follows.

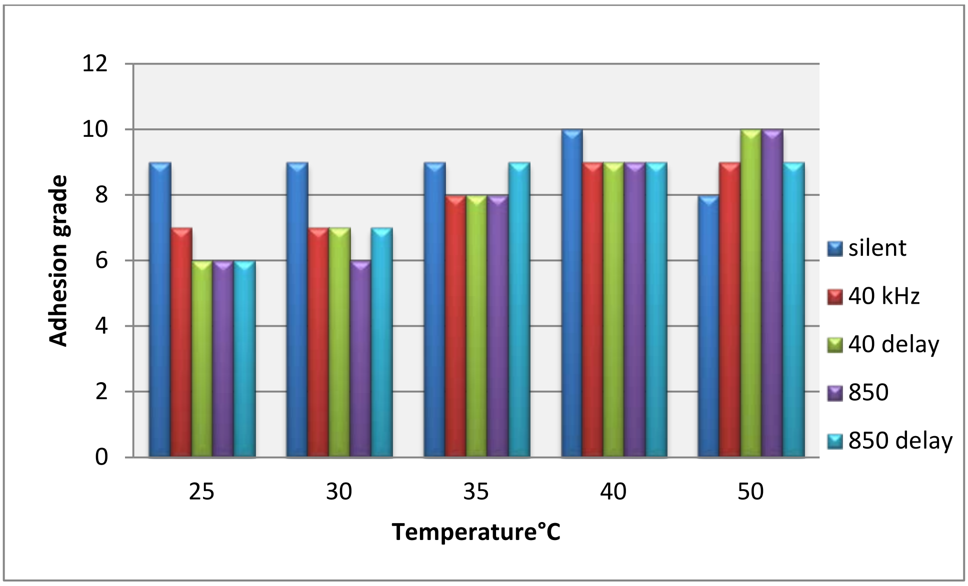


Figure (48) Adhesion grade at different temperatures at silent, 40 kHz and 850 kHz with and without delay time

There is a very slight increase in adhesion observed with a temperature increase however on the whole adhesion appears to be similar for ultrasonic and the delayed ultrasonic experiments with more variability observed at 50 °C. Adhesion does not appear to be dependent upon ultrasonic use or its delay.

## 3.10 Stability test of the electroless copper solution

To further understand the effect of ultrasound on the stability of the electroless copper baths experiments were carried out in order to determine how stable the electroless copper baths are. Printed circuit board manufacturers employ the same electroless copper plating baths for more than 6 month durations and during this period the copper bath must be kept stable for every single plating procedure (Coombs 1988). The copper plating bath consists of distilled water 811 ml per Litre, EDTA 150 ml per litre, Sodium hydroxide 23 ml per litre, formaldehyde 10 ml per litre and copper chloride 10 ml per litre. EDTA is added at 15% into the copper solution to prevent copper precipitation.

This section shows the effect on the electroless copper bath of applying ultrasound during the deposition process. Four epoxy test coupons were processed through the electroless copper bath. At the end of the plating cycle the bath was analysed by measuring the UV absorbance and the copper, formaldehyde and sodium hydroxide were replenished to their optimum values (See section 2.6). A further set of test coupons were then plated in the solution. At the end of this plating cycle the UV spectrophotometer absorbance was measured to give an indication of the copper remaining in the bath (See section 2.6). The solution was then left to stand for 24 hours in a suitable place at room temperature when another subsequent spectrophotometer absorbance measurement was taken. The difference in absorbance therefore gives an indication of the copper consumed or precipitated on the bottom of the beaker during this period which determines the stability of the bath.

### 3.10.1 Stability of conventional electroless copper plating

The UV absorbance for the electroless copper baths at silent condition was measured three times. Figure (49) shows these results at different temperatures and is compared to the zero time absorbance baths:

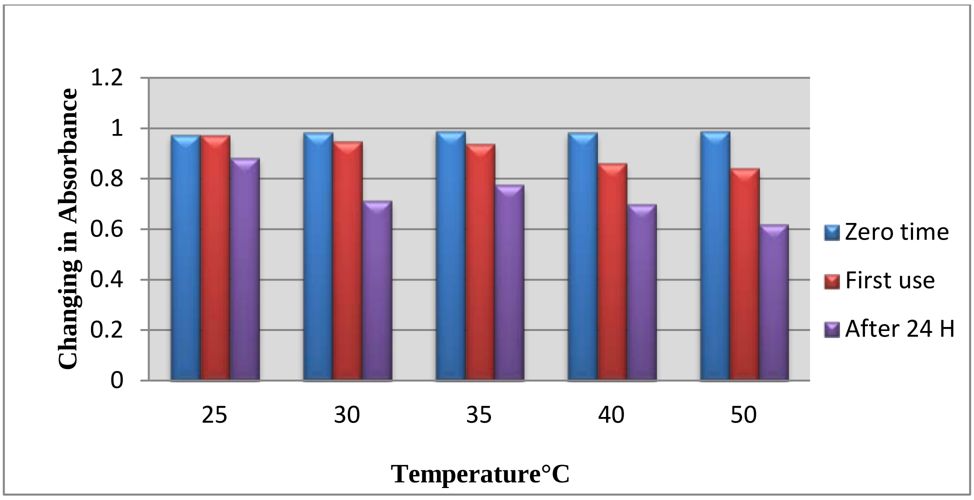


Figure (49) Effect of temperatures on the stability of electroless copper baths at silent condition

The figure above suggests that operating the electroless copper bath at higher temperatures reduces its stability particularly at a temperature of 40 and 50 $^{o}$C. At 25 $^{o}$C, a slight effect on the stability was noticed compared to the high temperature solution while a temperature of 30 $^{o}$C also produced results which showed a decreasing in the bath stability particularly after 24 hours.

### 3.10.2 Effect of ultrasound on the stability of electroless copper baths

The absorbance for the electroless copper baths after sonication with 40 and 850 kHz ultrasonic bath was measured three times at each different temperature. The Figure below shows these results at different temperatures and is compared to the absorbance of standard baths:

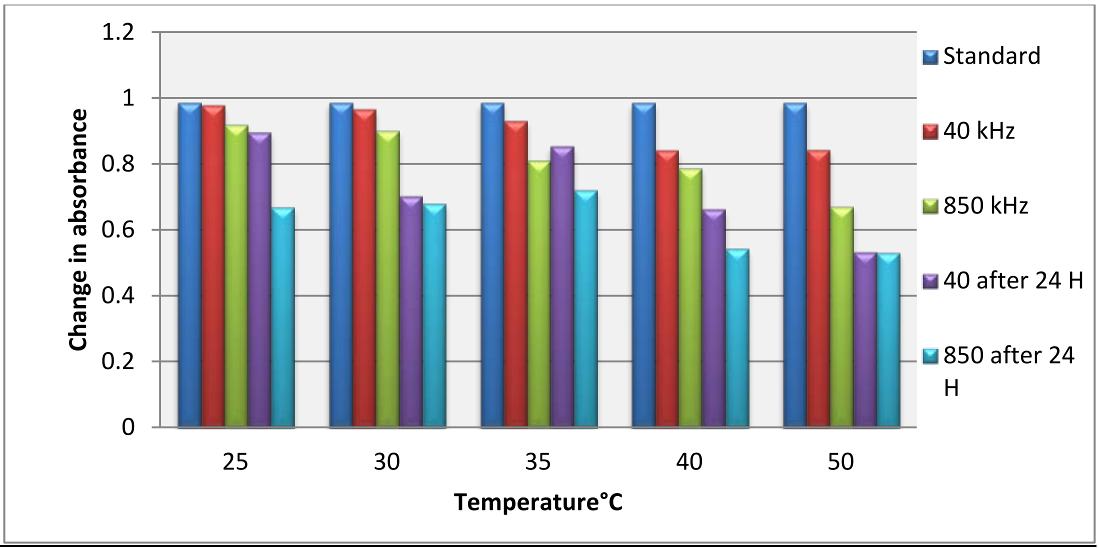


Figure (50) Effect of ultrasound on the stability of electroless copper baths at different temperatures

The absorbencies of the electrolesss copper bath after applying ultrasound for 25 minutes are exhibited in the figure (50). It is noticed that applying ultrasound at a frequency of 40 kHz has reduced the stability of the bath at all the different temperatures. The most noticeable stability reduction was observed at a temperature of 40 $^{o}$C and 50 $^{o}$C respectively. For all experiments, the stability of the baths was decreased after 24 hours. Applying ultrasound at the frequency of 850 kHz reduced the stability of the bath the highest amount. For all experiments, the stability of the baths was decreased even more after 24 hours.

Figure 51 below indicates the effect of ultrasound on an electroless plating bath where the copper is clearly seen at the base of the beaker having dropped out of solution due to the effect of sonication.

Figure (51) Effect of ultrasound on the electroless copper bath

### 3.10.3 Effect of delay time on the stability of electroless copper baths

The absorbance for the electroless copper baths after 7 minutes delay and then sonicated with 40 and 850 kHz ultrasonic baths was measured three times at each different temperature. The figure below shows these results at different temperatures and is compared to the absorbance of standard baths.

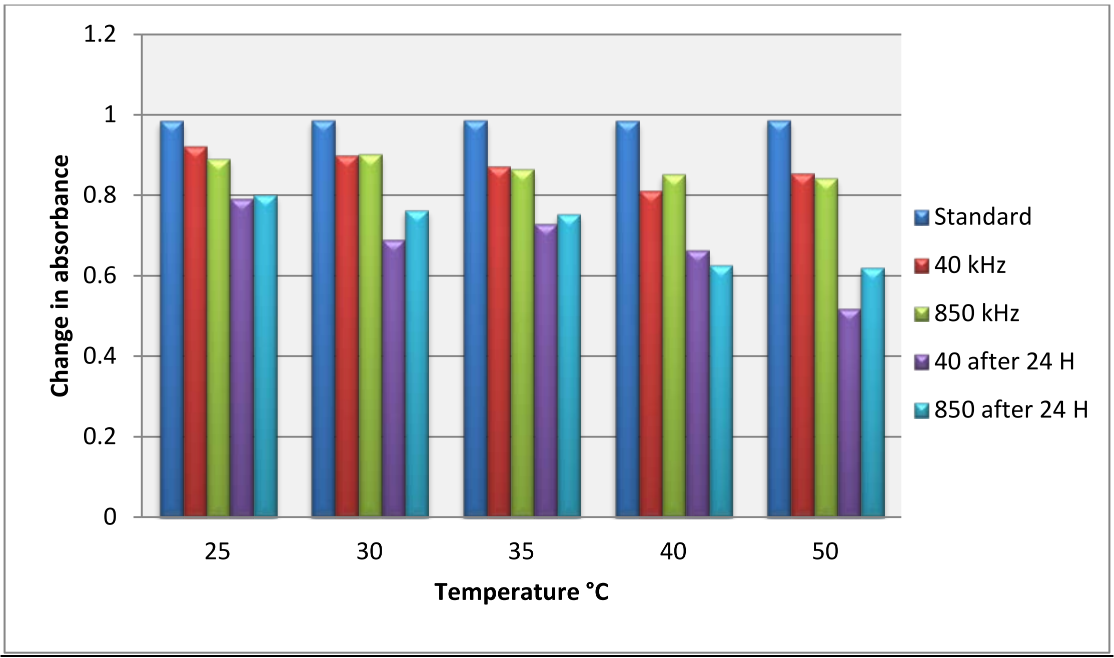


Figure (52) Effect of delay 7 minutes on stability of electroless copper baths at different temperatures

The absorbencies of the electrolesss copper bath are exhibited. Again re-use of the bath reduces its stability after first use, 24 hr use and over all temperatures. The greatest reduction in stability is observed for 850 kHz at higher temperatures with ultrasound not being of any benefit to stability at all. Introducing a 7 minute delay also reduces the stability of the plating baths slightly (compare with figure 51 above). This was expected as the plating rate associated with a 7 minutes delay is higher therefore more copper is consumed and a reduced absorbance results.

### 3.10.4 Effect of air bubbling on stability of electroless copper baths

The absorbance was measured for the electroless copper bath sonicated at 40 and 840 kHz with added air bubbling. Three measurements were taken at each individual temperature after first use and after 24 hours. Figure (53) shows these results at different temperatures and is compared to the standard absorbance for the electroless copper baths at the same temperatures:

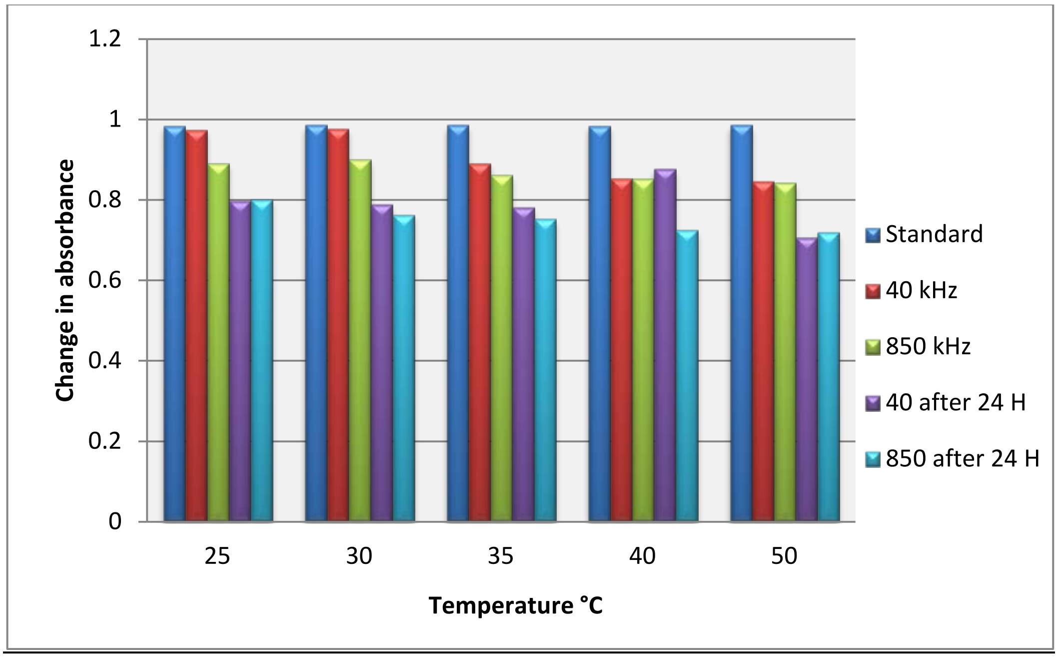


Figure (53) Effect of air bubbling on the stability of electroless copper baths at different temperatures

Applying air bubbling to the bath does not improve its stability with results being obtained which are very similar to those when using a 7 minute delay (no air bubbling – see figure 52 above). Use of additional air is therefore not of any benefit when attempting to stabilise a plating bath as the use of ultrasound destabilises it beyond recovery. All experiments showed that the stability of the baths was reduced more after 24 hours particularly at a temperature of 50°C. The stability of the 850 kHz baths was most reduced at all temperatures as previous results have also shown. Introducing air bubbling increased the stability of the bath slightly. Silent and 40 kHz experiments are more stable than 850 kHz. Air bubbling has been used as a stabilizer for electroless copper plating baths (Hanna, Hamid and Aal, 2004). In their work, using air bubbling has increased the breakdown time compared to no air bubbling as air is frequently bubbled through electroless copper baths in order to oxidize any copper species formed and thus avoid bath decomposition via copper disproportionation.

All the results obtained in this part of the project have shown clear evidence that at all different ultrasonic frequencies, silent conditions and different temperatures, the stabilities of the baths were reduced after first use. Moreover this effect is increased even further when the baths are re-used after 24 hours of first use.

Some of the results were anticipated as the normal electroless plating process leads to plating of the metal onto the surface of the substrate. This means that the copper component of the bath would have been removed from the solution and plated over the surface of the substrate. As a direct result of the plating process the electroless bath loses some of the concentration of its elements and therefore, the absorbance is reduced which is normal.

All the absorbencies produced by 850 kHz were lower than those obtained with 40 kHz and both frequencies produced absorbencies lower than silent conditions. This means that ultrasound is breaking the copper solution down by breaking the EDTA bond to the metal ion. At 850 kHz you would expect more radicals to be produced which could be destroying the EDTA, or the stabilizers, and therefore reducing the stability of the bath. The UV results above suggest that ultrasound destroys the copper solution within a short time.

# 4. Conclusion and Further work

## 4.1 Conclusion

The prime objective of this research work was to investigate the ability of ultrasound to increase the plating rate of electroless copper plating on an epoxy resin surface at lower temperature. It is well known that electroless copper plating is involved in a large number of electronic manufacturing processes which use this process within their production. The effectiveness of ultrasound is mainly attributed to a few factors. One of these factors is the ability of ultrasound to induce microjetting which could have an influence in increasing the electroless copper plating rate via thinning of the diffusion layer, which leads to enhancing the plating reaction. Another influence that is introduced by ultrasound is the production of free radicals. These are involved in the oxidation reaction which occurs on the epoxy surface during copper plating. Mass transport is another effect generated via ultrasound as this causes an increase in the movement of copper ions towards the epoxy surface. Sonication of the electroless copper solution also introduces a fine grain metal structure on the epoxy surface and this subsequently produces good surface coverage by the plated metal, thus aiding corrosion resistance.

Applying 40 kHz sonication at low temperatures has not shown significant results in term of increasing the plating rate compared to the results obtained using the silent electroless plating process at 35 ºC. However at slightly higher temperatures of 45 ºC and 50 ºC the plating rate was slightly increased. Using 850 kHz sonication however did not introduce any noticeable results in terms of increasing the copper plating rate at most of the temperatures examined.

The best plating rate improvement was noticed when 7 minutes delay was applied prior to introducing sonication during the plating process. When using the 40 kHz ultrasonic bath the plating rate was higher than that obtained under silent conditions at most of temperatures employed, except at a temperature of 25 ºC and 30 ºC.. When using a frequency of 850 kHz an improvement was shown on the plating rate but the results were not as significant as those observed when a 40 kHz bath was utilized. 850 kHz particularly showed a reduced plating rate at a temperature of 50 ºC.

Using air bubbling when applying a 7 minutes delay during the electroless copper plating has not shown an improvement on the plating rate. For this part of the research work, using the delay concept, with frequencies of 40 kHz and 850 kHz, results showed a decrease of the plating rate compared to plating values without the air bubbling.

Glyoxylic acid was utilized instead of the formaldehyde as a reducing agent and a 7 minutes delay technique was applied. The results showed a much lower plating rate compared to the results when using formaldehyde as reducing agent. Both frequencies of 40 kHz and 850 kHz produced a reduction in the plating rate in contrast to the results obtained at the same conditions but with using formaldehyde.

Regarding the stability of the electroless copper bath, all the results have indicated that the stability of the bath was reduced after the first use and was reduced even more after 24 hours. However, applying ultrasound at frequencies of 40 kHz and 850 kHz has further decreased the stability of the bath compared to the stability of the silent bath. Applying 850 kHz sonication has reduced the stability of the electroless copper bath more than applying 40 kHz. At both frequencies, the stability of the bath was higher in the absence of any sonication delay time. This was expected as using the delay method introduced a higher plating rate and therefore, more copper was consumed from the electroless copper bath. Additional air bubbling stabilised the baths and this was accepted as the plating rate achieved in this part of work was lower than the results achieved with using ultrasound and the delay method. These results were corroborated with the stability results which meant that less copper metal has been consumed or plated on the substrate surface.

In conclusion the best plating rates were achieved when a delay of 7 minutes was utilized before applying ultrasound. Air bubbling had reduced the plating rate and has little beneficial effect on the copper bath stability. Using glyoxylic acid produced very poor plating rates when compared to formaldehyde and sonication aids the destablilisation of the electroless plating baths.

## 4.2 Further work

For further comparisons to find the optimal conditions for the use of ultrasound during electroless copper plating there are particular areas which would be very interesting to investigate such as:

- Further investigation into the use of an ultrasonic probe which has a frequency of 20 kHz, since it has been proved that ultrasound at this frequency can be effective for copper plating. It has been confirmed that the generation of radicals depends on frequency and power used; 20 kHz produces less radicals than higher frequencies such as 850 kHz but introduces more physical/mechanical benefits.

- Examining the effect of ultrasound and temperature on coverage by measuring the copper thickness layer which is plated on the epoxy samples. Enhanced plating rate may not lead to even coverage of copper on the substrate surface and by examining the actual thickness of the coating at several points this could determine the extent of coating across the surface of the epoxy.

- Further extensive SEM and Adhesion tests at various temperatures would be beneficial in determining grain sizes and adhesion.

- Catalyst coverage using XPS could be examined but at different frequencies, such as 850 kHz. This would determine if the removal effect is lower at higher frequencies.

- Further investigation into using very high sonication frequencies such as 1000 kHz which could generate more free radicals involved in the oxidation process. These free radicals may form more chemical bonds between the substrate and the copper and may aid the electroless plating reaction at the surface. This enhancement of the cavitational influence could produce a more desirable surface treatment for improving copper adhesion at the higher frequencies.

## REFERENCES

Anik, T., Ebn Touhami, M., Himm, K., Schireen, S., Belkhmima, R.A., Abouchane, M and Cisse, M. (2012) ‘Influence of pH Solution on Electroless Copper Plating Using Sodium Hypophosphite as Reducing agent’. *Int. J. Electrochem. Sci.,7. 2009*-2018

Briggs, D. (1998) *surface analysis of polymers by XPS and static SIMS*. Cambridge, the press syndicate of the University of Cambridge, 1-2

Bulasara, V. K., Abhimanyu, M. S., Pranav, T., Uppaluri, R. and Purkait, M. K. (2012) ‘Performance characteristics of hydrothermal and sonication assisted electroless plating baths for nickel–ceramic composite membrane fabrication’. *Desalination, 284*(0), 77-85.

Carcel, J. A., Benedito, J., Bon, J. and Mulet, A. (2007) ‘High intensity ultrasound effects on meat brining’. *Meat Science, 76*(4), 611-619.

Cheng, D. H., Xu, W. Y., Zhang, Z. Y. and Yiao, Z. H. (1997) ‘Electroless copper plating using hypophosphite as reducing agent’. *Metal Finishing, 95*(1), 34-34.

Coombs, C. F. (1988) *Printed Circuits Hand book*, United State of America, McGraw-Hill (1988), 1-02

Cobley, A, J. and Saez, V (2012) ‘The use of ultrasound to enable low temperature electroless plating;. *Circuit World 38/1*, 12-15.

Cobley, A. J., Mason, T. J., Alarjah, M., Ashayer, R., and Mannan, S. H. (2011) 'The Effect of Ultrasound on the Gold Plating of Silica Nanoparticles for use in Composite Solders'. *Ultrasonics Sonochemistry* 18 (1), 37-41

Cobley, A. J., Mason, T, J. and Robinson, J. (2008) ‘Sonochemical Surface Modification: A Route to Lean, Green and Clean Manufacturing? ’. *journal of Applied Surface Finishing,* 3**,** 190-196

Cobley, A. and Mason, T. (2008) ‘The sonochemical surface modification of materials for electronic manufacturing’. The effect of ultrasonic source to sample distance. *Circuit World*, 34**,** 18-22.

Cobley, A. (2007) ‘Alternative surface modification processes in metal finishing and electronic manufacturing industries’. *Transactions of the Institute of Metal Finishing*, 85**,** 293-297.

ECVV (2011) *Electronic Balance* [online]- available from < http://www.ecvv.com > [ 09 December2011**]**

Fadley, C. S. (2010). X-ray photoelectron spectroscopy: Progress and perspectives. *Journal of Electron Spectroscopy and Related Phenomena, 178-179*, 2-32.

Gan, X., Wu, Y., Liu, L., Shen, B. and Hu, W. (2007) 'Electroless copper plating on PET fabrics using hypophosphite as reducing agent'. *Surface and Coatings Technology, 201*(16-17), 7018-7023.

Gibson, J. H., Hon, H., Farnood, R., Droppo, I. G. and Seto, P. (2009) 'Effects of ultrasound on suspended particles in municipal wastewater'. *Water Research, 43*(8), 2251-2259.

Goosey, M. and Poole, M. (2004) 'An introduction to high performance laminates and the importance of using optimised chemical processes in PCB fabrication'. *Circuit World*, 30**,** 34-39

H.T.F.C (2007) *How To Fix Computers* [online]- available from < http://www.howtofixcomputers.com > [2011**]**

Hanna, F., Hamid, Z. A. and Aal, A. A. (2004) 'Controlling factors affecting the stability and rate of electroless copper plating'. *Materials Letters, 58*(1-2), 104-109.

He, Y., Grieser, F. and Ashokkumar, M. (2011) 'The mechanism of sonophotocatalytic degradation of methyl orange and its products in aqueous solutions'. *Ultrasonics Sonochemistry, 18*(5), 974-980.

Hu, Y., Guanghui, H, Xiaoling, C., Xiaoting, X., Haiyan, Z., Feng, L. and Qingsong, X. (2011). Study on the Effect Waves on the Low Temperature Electroless Ni-P Plating on Copper Substrate. *Advanced Materials Research 189-193*, 1142-1145.

Huang, Z., Xie, F. and Ma, Y. (2011) 'Ultrasonic recovery of copper and iron through the simultaneous utilization of printed circuit boards (PCB) spent acid etching solution and PCB waste sludge'. *Journal of Hazardous Materials, 185*(1), 155-161.

Hwangbo, Y. and Song, J. (2011) 'Plastic deformation behavior analysis of an electrodeposited copper thin film under fatigue loading'. *International Journal of Fatigue, 33*(9), 1175-1181.

Katsuam, K. (1995) *Anodizing Process.* United States Patent 5,401.382. Mar 28, 1995

Kobayashi, K., Chiba, A. and Minami, N. (2000) 'Effects of ultrasound on both electrolytic and electroless nickel depositions'. *Ultrasonics, 38*(1-8), 676-681.

Lee, M, C., Lee. M, H., Hur. J, Y., Lee. H, N. and Lee, H, K. (2011) 'Ultrasound-Assisted Pd Activation Process for Electroless Silver Plating'. *World academy of Science, Engineering and Technology 59* . 1079-1081.

Lu, Y. (2009) 'Electroless copper plating on 3-mercaptopropyltriethoxysilane modified PET fabric challenged by ultrasonic washing'. *Applied Surface Science, 255*(20), 8430-8434.

Lu, Y., Jiang, S. and Huang, Y. (2010) 'Ultrasonic-assisted electroless deposition of ag on PET fabric with low silver content for EMI shielding'. *Surface and Coatings Technology, 204*(16-17), 2829-2833.

Lynnworth, L (1974) ' Industrial Application of Ultrasound-A Review II.

Meaurement, Test and Process Control Using Low-Intensity Ultrasound'. *IEEE*

*Transactions of Sonics and Ultrasonics*. November 1974

MMRC (n.d.) *X-ray photoelectron spectroscopy (XPS) Analyser* [online]- available from < http://mmrc.caltech.edu/ > [11 January 2012]

Mallik, A. and Ray, B. C. (2009) 'Morphological study of electrodeposited copper under the influence of ultrasound and low temperature'. *Thin Solid Films, 517*(24), 6612-6616.

Mandich, N. V. (1994) 'Chemistry of Solvent Conditioning Prior to Permanganate Etching of PCB's'. *Transactions of the Institute of Metal Finishing,* 72**,** 41-44

Mason, T. J., Cobley, A. J., Graves, J. E. and Morgan, D. (2011) 'New evidence for the inverse dependence of mechanical and chemical effects on the frequency of ultrasound.' *Ultrasonics Sonochemistry, 18*(1), 226-230.

Mason, T. (1999) *Sonochemistry*, Oxford: Oxford University Press

Mason, T. and Lorimer, J. (2002) *Applied sonochemistry :the uses of power ultrasound in chemistry and processing*, Weinheim: Wiley-VCH GmbH

Mason, T. and Peters, D. (2002) *Practical sonochemistry :uses and applications of ultrasound*, 2nd edn. Chichester: Horwood Publishing Limited

Matsumoto, M., Allen, J., Yoshizawa, S., Ikeda, T. and Kaneko, Y. (2005) 'Medical ultrasound with microbubbles'. *Experimental Thermal and Fluid Science*. 29 255–265

Mkhlef, B. (2010) *An evaluation of solvents conditions to increase cavitational effects of power ultrasound for the surface treatment of a range of materials used in the many of PCBs/electronic industry*. Published MSCR thesis. Coventry: Coventry University

Nano Lab (2009) *Ultrasonic Probe Dispersion Equipment* [online]- available from < http://www.nano-lab.com/ultrasonic-probe-dispersion-equipment.html> [13 January 2012]

Ohsaka, T., Isaka, M., Hirano, K. and Ohishi, T. (2008) 'Effect of ultrasound sonication on electroplating of iridium'. *Ultrasonics Sonochemistry, 15*(4), 283-288.

Paniwnyk, L., & Cobley, A. (2010). Ultrasonic surface modification of electronics materials. *Physics Procedia, 3*(1), 1103-1108.

Poyner, J.A. (1988) *Electroplating*, Hertford Shire 2.

Printed circuit board (n.d.) *Printed Circuit Board: The making of the Substrate and Plating the Holes* [online]- available from < http://printedcircuitboard.blog.com/ >[19 November 2011]

Rehorek, A., Tauber, M. and Gübitz, G. (2004) 'Application of power ultrasound for azo dye degradation'. *Ultrasonics Sonochemistry, 11*(3–4), 177-182.

Ruo, F., Yiyun, Z. and Ciguang, B. (1997) 'Sonochemistry in china'. *Ultrasonics Sonochemistry, 4*(2), 183-187.

Shinka Industry (n.d.) *Multi Frequency Sonoreactor SRM* [online] available – from < http://www.shinka-sangyo.co.jp/SRM-eng.html>, [09 November 2011]

Siau, S., Vervaet, A., Van Calster, A., Swennen, I. and Schacht, E. (2004) 'Epoxy polymer surface roughness modeling based on kinetic studies of wet chemical treatments'. *Journal of the Electrochemical Society*, 15

Sone, M., Kobayakawa, K., Saitou, M. and Sato, Y. (2004) 'Electroless copper plating using FeII as a reducing agent'. *Electrochimica Acta, 49*(2), 233-238.

Su, W., Yao, L., Yang, F., Li, P., Chen, J. and Liang, L. (2011) 'Electroless plating of copper on surface-modified glass substrate.' *Applied Surface Science, 257*(18), 8067-8071.

Tian, Q. and Guo, X. (2010) ‘Electroless copper plating on microcellular polyurethane foam’. *Transactions of Nonferrous Metals Society of China, 20*(Supplement 1), s283-s287.

Tonanasia (2009) – *Gloss meter* [online] available – from< http://www.tonanasia.com/gloss_meter_spec.php?id_prd=356> ,[ 12 January 2011]

Touyeras, F., Hihn, J. Y., Bourgoin, X., Jacques, B., Hallez, L. and Branger, V. (2005) ‘Effects of ultrasonic irradiation on the properties of coatings obtained by electroless plating and electro plating’. *Ultrasonics Sonochemistry, 12*(1-2), 13-19.

Touyeras, F., Hihn, J. Y., Delalande, S., Viennet, R., & Doche, M. L. (2003). Ultrasound influence on the activation step before electroless coating. *Ultrasonics Sonochemistry, 10*(6), 363-368.

Touyeras, F., Hihn, J. -., Doche, M. -. and Roizard, X. (2001) ‘Electroless copper coating of epoxide plates in an ultrasonic field’. *Ultrasonics Sonochemistry, 8*(3), 285-290.

UltraWave (2012) *Ultra Analogue Benchtops Baths* [online] available – from < http://www.labsource.co.uk/shop/ultra-analogue-benchtops-baths-c-4_190.html> , [ 15 February 2011]

Wang, L., Sun, L. and Li, J. (2011). Electroless copper plating on fraxinus mandshurica veneer using glyoxylic acid as reducing agent. *BioResources 6(3),* 3493-3504.

Walker, R. (1997) ‘Ultrasound improves electrolytic recovery of metals’. *Ultrasonics Sonochemistry, 4*(1), 39-43.

Wu, X. and Sha, W. (2009) ‘Experimental study of the voids electroless copper deposits and the direct measurement of the void fraction based on the scanning electron microscopy images’ *Applied Surface Science*. 255, 4259-4266

Zhao, Y., Bao, C., Feng, R. and Chen, Z. (1995) ‘Electroless coating of copper on ceramic in an ultrasonic field’. *Ultrasonics Sonochemistry,* 2**,** S99-S103

Zhao, Y., Bao, C., Feng, R. and Le, R. (1998a) ‘A New Method of Etching ABS Plastic for Plating by Ultrasound’. *Plating and Surface Finishing,* 85**,** 98-100