Thin Solid Films 597 (2015) 226–230

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

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

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

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

ARTICLE INFO

Article history:
Received 5 June 2015
Received in revised form 19 November 2015
Accepted 25 November 2015
Available online 28 November 2015

Keywords:
Ultrasound
Sonochemistry
Electroless
Copper
Deposition rate
Porosity
Palladium
Printed circuit boards

ABSTRACT

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

1. Introduction

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

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

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

* Corresponding author.
E-mail address: a.cobley@coventry.ac.uk (A.J. Cobley).

http://dx.doi.org/10.1016/j.tsf.2015.11.068
0040-6090/

the relevance of these studies to real manufacturing environments has to be questioned.

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

2. Experimental details

2.1. 'Self-accelerating' electroless Cu plating process

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

2.2. Experimental setup

All the experiments conducted in 'silent conditions' (i.e. absence of ultrasound) were carried out in a 1000 mL beaker containing 800 mL of the Cu 3350-1 solution continuously stirred with a magnetic stirrer, whereas a 40 kHz 375 TT ultrasonic bath (Langford Electronics UK Ltd) containing 1000 mL of the Cu 3350-1 solution was used in the experiments with ultrasound. The bath was previously characterized by calorimetry [19], showing an ultrasonic power of 0.103 W/cm^3. All the experiments were conducted on test coupons (2.5 × 2.5 cm) prepared from Isola Duraver 104 sheets, a typical PCB laminate material.

2.3. Experimental procedures

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

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

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

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

$$t = \frac{\Delta m}{Ap} \quad (1)$$

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

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

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

For the investigation into the effects of low-frequency sonication on the Pd–Sn activated dielectric material the test coupons underwent the whole process described in Table 1 except for the Circuposit Electroless Copper 3350-1, where a 'simulated' 3350-1 bath under silent conditions and ultrasound was used instead. The 'simulated' electroless Cu solution contained all the elements of the electroless Cu solution except the Cu-containing component to ensure that coupons were not coated with Cu as this would prevent analysis of the Pd content on the surface of the substrate. X-Ray Photoelectron Spectroscopy (XPS) analysis was used to determine the amount of Pd and Sn on the surface of the test coupons after being immersed in the 'simulated' 3350-1 bath for 10 min with/without the presence of ultrasound. XPS analysis was conducted in a Thermofisher ESCALAB 250 electron spectrometer equipped with a hemispherical sector energy analyzer.

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

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

3. Results and discussion

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