CHEMICAL ENGINEERING TRANSACTIONS
VOL. 41, 2014
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Simonetta Palmas, Michele Mascia, Annalisa Vacca

ISBN 978-88-95608-32-7; **ISSN** 2283-9216
DOI: 10.3303/CET1441007

Electrodeposition of Copper Patterns Using EnFACE Technique under Ultrasonic Agitation

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A micro-scale pattern transfer method, the Enface technique, has been developed for metal plating and etching. The method involved a patterned tool and substrate brought together in close proximity and a current is passed or voltage is applied between them, enabling metal to be deposited or removed from the substrate selectively. The process requires sufficient electrolyte agitation within an inter-electrode gap of 0.03 cm and has been previously shown to hold in a vertical flow cell, however, for the process to be adapted for tank-type systems for industrial implementation scale-up of agitation is required. It is known that ultrasonic waves can enhance mass transfer during metal electrodeposition. It has therefore been proposed that the use of ultrasonic waves would be an appropriate agitation method for this geometry.
A 20 kHz ultrasonic probe has been shown previously to provide agitation to improve the mass transfer within an inter-electrode gap 0.15 cm during copper electrodeposition in a 500 ml cell (Coleman and Roy, 2014). This same system was used to deposit 4 µm thick features under direct current plating on nickel using an anode with a 1 x 5 mm rectangle feature using a 0.1 M $CuSO_4$ electrolyte. Potential responses were recorded to interrogate the stability of plating conditions, with and without agitation. It was found that at 50% of the limiting current deposited under silent conditions cell potential was less stable and the width of the feature was ~800 µm larger than the tool. It was found that plating using long current pulses with bursts of ultrasound during the off-time provided the most stable potential response, reduced the deposit roughness and improved the adherence of the copper feature to the substrate.

1. Introduction

Microfabrication technologies require methods of patterning substrates to fabricate such devices as MEMS, microfluidics and micro-optic systems (Franssila, 2010; Madou, 2012). The most common microfabrication process is photolithography, which requires each substrate to be coated with a photoresist layer, which is then exposed to ultraviolet light through a mask with the desired pattern to be transferred. The photoresist is then developed leaving a pattern of exposed substrate areas, which can then be either etched or deposited, after which it is removed from the surface by dissolving in an appropriate solvent (Franssila, 2010; Madou, 2012).
Although photolithography is well understood, it is a multistep process and is, therefore, expensive. In addition, it requires the use of hazardous chemicals and produces a lot of waste products. Cheaper and more environmentally friendly microfabrication processes are therefore being developed to micropattern surfaces. One such method is Enface (Schönenberger and Roy, 2005; Roy, 2007), an electrochemical process that uses a patterned tool placed in close proximity to the substrate, allowing metal to be selectively etched (Schönenberger and Roy, 2005) or deposited (Wu et al., 2011) when a voltage is passed between them. This therefore eliminates the need for applying a photoresist mask to the substrate and also the removal of this mask for each substrate.
Previously, a vertical flow cell was used to etch (Schönenberger and Roy, 2005) or deposit (Wu et al., 2011) copper pattern features, 5-100 µm in size. Later pattern transfer within a tank-type geometry was investigated, where nickel patterns of 1 mm x 5 mm and features of 300-800 µm were deposited

Please cite this article as: Coleman S., Roy S., 2014, Electrodeposition of copper patterns using enface technique under ultrasonic agitation, Chemical Engineering Transactions, 41, 37-42 DOI: 10.3303/CET1441007

(Widayatno and Roy, 2014). It was found that the mass transfer of ionic species within the narrow inter-electrode gap was insufficient, high-lighting the importance requirement of providing adequate agitation.
Ultrasonic (US) agitation is known to improve stirring in electrochemical systems due to the intensity of the flow of US waves and also the movement and oscillation of cavitation bubbles (Compton et al., 1996; Walton et al., 1995). US has also previously been shown to increase copper deposition rates (Kaufmann et. al, 2009). A previous investigation by our group established two key principles: (1) that mass transfer within a narrow electrode gap during copper deposition was significantly improved (Coleman and Roy, 2014), (2) a mass transfer correlation for US in this cell system.
For Enface technology using photolithography, however, the collapse of cavitation bubbles at a solid surface can result in a phenomenon known as micro-jets (Benjamin and Ellis, 1996) which can cause pitting on the metal deposit surface (Jensen et. al, 2003) as well as remove photo resist. In this work, we have developed a comprehensive study on the use of US agitation during the electrodeposition of copper patterns under Enface conditions to determine if the process is advantageous and allows pattern transfer using a tool using standard resist technology.

2. Experimental

Plating experiments were carried out in a 500 ml cylindrical PVC cell (figure 1) with 1 cm diameter polished electrodes facing each other, with a distance of 0.03 cm between them, measured using a spacer. The anode and cathode were copper and nickel discs respectively and a solution of 0.1 M $CuSO_4$ was used as an electrolyte. The electrodes were prepared by polishing with SiC paper with grit size #2400 and then #4000, before rinsing with deionized water. The copper anode tools were prepared by masking them with a non-conductive material (Kapton tape). A blade was then used to cut out a 1 x 5 mm rectangle from the tape, leaving an exposed area of copper with a tolerance of ±0.075 mm in width.
An *Eco Chemie Autolab Potentiostat (PGSTAT30)* was used to apply direct current (DC) galvanostatically for pattern transfer plating, and also used for some limiting current experiments to identify what currents to apply for plating. *NOVA 1.7* software was used to input the settings for plating experiments and also recorded the response data. For DC plating, a chronopotentiometry procedure was set up to apply the desired current; these DC experiments were carried out either under silent conditions or with constantly applied US agitation. When applying long current pulses an automatic procedure was set-up in *NOVA* which involved alternating chronopotentiometry procedures with periods where no current was applied, therefore creating a series of long current pulses. When plating with 50% of the limiting current (i_{Lim}) and 75% i_{Lim}, three chronopotentiometry procedures were applied, each with a time of 200s and 150s respectively, and both with a current off-time of 25s

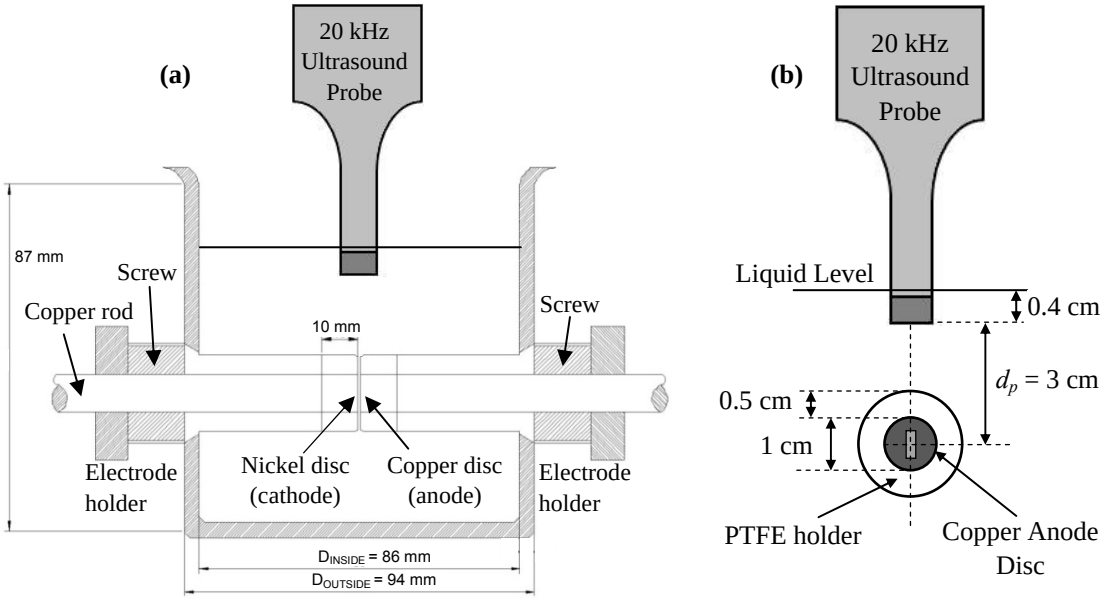

Figure 1 – (a) Side-view of experimental set-up of the electrochemical cell used in this work. (b) Frontal-view of anode surface; dark grey circle = Masked area; light grey rectangle = Area of exposed copper

When combining long current pulses with ultrasonic agitation, the ultrasound source, described below, was switched on and off manually and applied for 10s at the start of each off-time.
A *SONICS Vibra-Cell VC505 Processor* connected to a 20 kHz ultrasound probe with a 1.3 cm diameter titanium alloy tip was used to apply ultrasonic agitation, operating at a power (p) of 9 W/cm^2. The probe tip was submerged into the solution by 0.4 cm and was placed above the gap, side-on to the electrode gap with a probe-electrode distance (d_p) of 3 cm. Profilometries of the copper deposits were measured across the centre of the feature using either a *Dektak Profilometer* or a *Tencor P-1 Long Scan Profilometer*.

3. Results and Discussion

Initially, some limiting current experiments were carried out under conditions required during the Enface process; with a 0.03 cm electrode gap using a dilute 0.1 M CuSO4 electrolyte solution and a 1 x 5 mm rectangle of exposed anode area, used to choose currents for the deposition experiments. The limiting current density increased by a factor of 3 under US agitation ($i_{Lim,US}$) at 9 W/cm2 at a probe-electrode distance of 3 cm compared to silent conditions, therefore illustrating a significant increase in mass transport of ions when ultrasound is induced in an Enface system, investigated in more detail in a previous paper (Coleman and Roy, 2014).

3.1 Potential response during DC deposition with US agitation

The potential responses during silent DC deposition of 1 x 5 mm copper features are shown in lines 1a and 1b in figure 2. Each response shows the typical potential peak that is present just after the current is applied which is evidence of the charging of the double layer. Several repeats of these DC current plating experiments showed that a decrease in cell potential (indicated by the arrows in figure 2(a) occurred at 394 ±20 seconds and 122 ±55 seconds with applied currents of 50% i_{Lim} and 75% i_{Lim} respectively.
The ratio of these times for each current is 1:3.23. This was found to be similar to the ratio of transition times (τ_i) for each current, 1:2.25, calculated using the Sand equation, shown in equation 1 (Sand, 1901).

$$\tau_i = \frac{\pi D_i n_i^2 F^2 c_{i,b}^2}{4 i_i^2} \quad (1)$$

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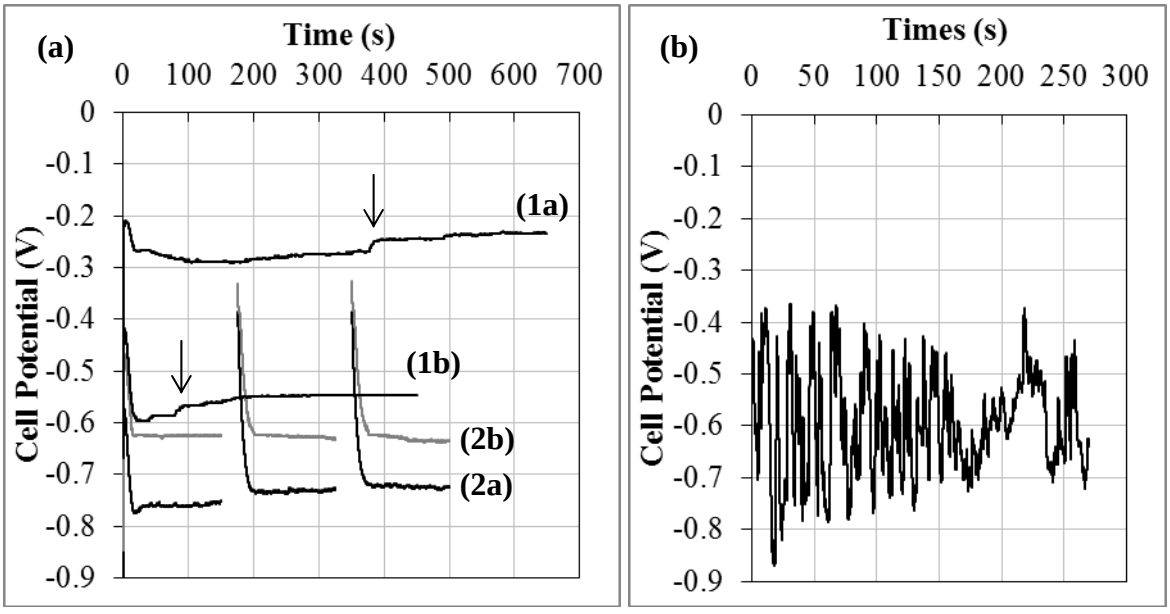

Figure 2 - Potential responses during galvanostatic plating with 1 x 5 mm of exposed anode area. (a) Line 1a. DC plating under silent conditions at -40 mA/cm^2 (50% i_{Lim}) for 650 s ; Line 1b. DC plating under silent conditions at -60mA/cm^2 (75% i_{Lim}) for 450 s ; 2a. Long current pulse plating under silent conditions at -60mA/cm^2 (75% i_{Lim}) with 150s on-time and 25s off-time ; 2b. Plated under the same conditions as for 2a but with a 10s burst of ultrasound during the off-time. d_p = 3 cm, p = 9 W/cm^2. (b) DC plating under constant ultrasound conditions at -100 mA/cm^2 (50% $i_{lim, US}$) for 270s with d_p = 3 cm, p = 9 W/cm^2.

where D_i is the diffuse ion coefficient, n_i is the number of electrons, F is the Faraday constant, $c_{i,b}$ is the concentration of Cu^{2+} ions in the bulk, and i_i is the plating current density.
The τ_i is the time from when current is applied until the Cu^{2+} ion concentration on the electrode-electrolyte interface becomes zero. Therefore, the similarity in these two ratios suggests that the drop in cell potential is related to the time taken for the Cu^{2+} ions within the narrow electrode gap to run out, due to insufficient ion replenishment from the bulk electrolyte solution outside the electrode gap towards the cathode surface within the gap.
When plating with DC current along with constant ultrasonic agitation, the potential fluctuated erratically, shown in figure 2(b). This is caused by the fully turbulent flow regime found to be present in these narrow ultrasound geometries (Coleman and Roy, 2014) and also cavitation bubble collapse.
Additionally, the bubbles also get entrapped between the electrodes, inhibiting further deposit growth in that area. It was also observed that etched copper from the anode got trapped within the narrow gap during silent deposition experiments, which would further contribute to restriction in convection flows. This observation may have also contributed to the slight discrepancy in the ratios mentioned above.
In view of these observations, short bursts of US were applied during the off-time of long current pulses in order to agitate the fluid within the electrode gap. Lines 2a in figure 2(a) show the potential response while plating a pattern feature using long 150s current pulses with a silent 25s off-time. The potential responses tend to be more stable when using long current pulses as opposed to DC. The steady-state potential reached after each current pulse is applied appears to be more constant when ultrasound bursts are induced during the off-time, illustrated by line 2b in figure 2(a). This is because of the relaxation of the diffusion layer which occurs during the off-time, allowing time for fresh Cu^{2+} ions to be transported from outside the gap to the electrode surface within the gap.

3.2 Deposit Characterisation

Figure 3 shows profilometry of copper deposits plated on a nickel substrate with a 1 x 5 mm rectangle of exposed copper anode surface

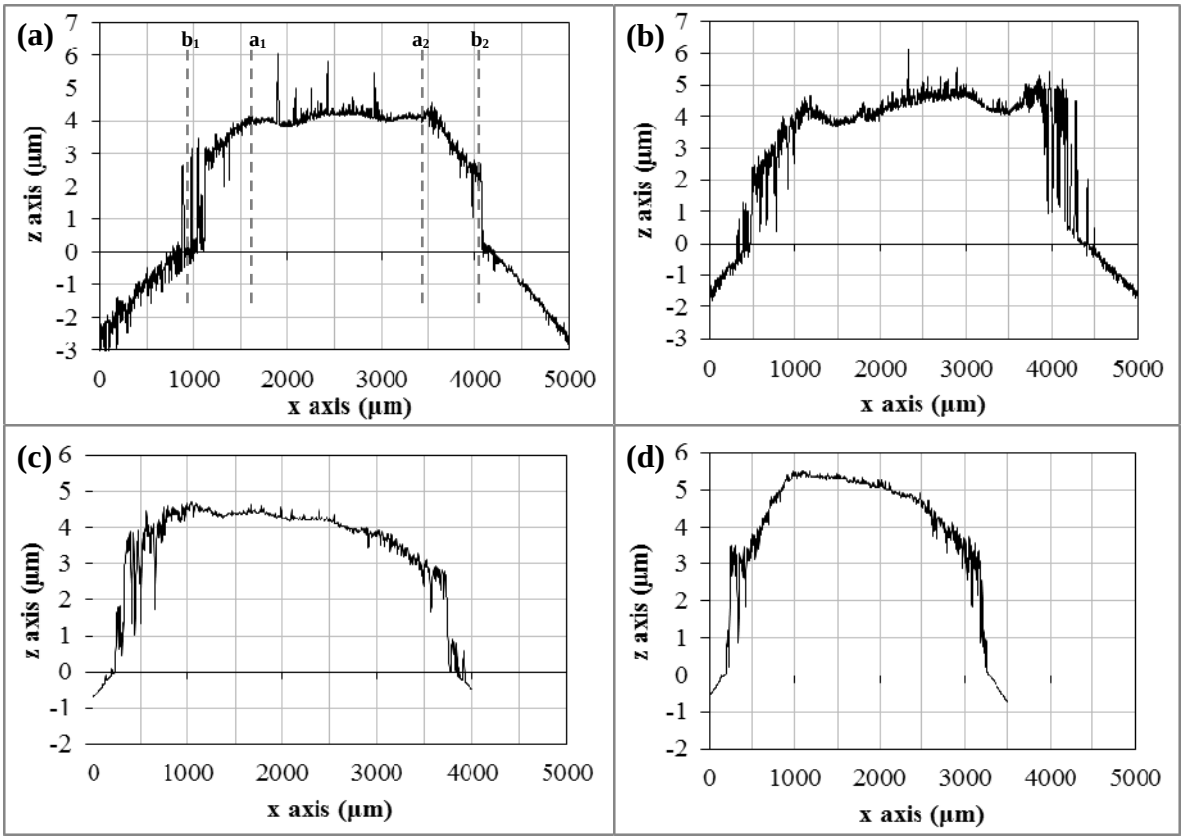

Figure 3 – Profilometry of deposited copper features on a nickel substrate with 1 x 5 mm of anode feature. (a) Silent DC plated at 50% i_{Lim} for 650s ; (b) Silent DC plated at 75% i_{Lim} for 450s ; (c) Silent long current pulse plating at 50% i_{Lim} with 200s on-time with 25s off-time ; (d) Long current pulse plating at 50% i_{Lim} with 200s on-time and a 25s off-time with 10s seconds of ultrasound during the off-time, p = 9 W/cm^2 , d_p = 3 cm.

In all the profiles, the very edges, at either side of the deposit, only appear to be steeply angled due to instrumentation issues.

The deposit shown in figure 3(a) was plated at 50% i_{Lim} under silent conditions; the thickness of the deposit is approximately 4 μm. There appears to be two distinct sections of the profile; a rough section at the edges (b_1-a_1 and a_2-b_2) and a smoother section in the middle (a_1-a_2). SEM images showed that regions b_1-a_1 and a_2-b_2 are actually a very thin rough layer of copper nuclei, thought to be due to current leaking at the edges of the Kapton tape mask. This observation means that the width of the deposit feature is closer to 1800 μm (distance 'a_1 – a_2') which is 800 μm wider than the anode feature size, caused by current spreading due to curvature in current lines.

The profile for the deposit pattern plated with 75% i_{Lim} under silent conditions is shown in figure 3(b). The roughness of the copper features were 1.87 μm and 2.84 μm for the deposits plated at 50% i_{Lim} and 75% i_{Lim} respectively. It is well known that as the plating current density reaches values closer to the mass transfer limiting current the surface roughness of the deposit increases (Ibl and Schadegg, 1967).

Figure 3(c) and 3(d) are profilometry of deposit features plated with long current pulses. The deposits plated under silent conditions (3c) and with US during the off-time (3d) have a roughness of 0.042 μm and 0.141 μm respectively, lower than the features deposited using silent DC. The slightly higher roughness of the deposit plated with ultrasound could possibly be attributed to effects of micro-jetting, which can result in pit formation in the deposit feature, a known issue caused by this micro-jetting phenomena (Jensen et al., 2003).

The current efficiency for the deposit plated at 50% i_{Lim} under silent DC plating conditions was 86%. The deposits plated using long current pulses, with and without US during the off-time, had current efficiencies of 98% and 91% respectively.

3.3 Discussion

It is interesting to note that when applying long current pulses under silent conditions the adherence of deposit to the nickel electrode surface was very poor, and often peeled off from the surface during rinsing with deionized water. This suggests that as plating proceeds there is a depletion of the Cu^{2+} causing a decrease in concentration of Cu^{2+} within the electrode gap, resulting in reduction of hydrogen. This would therefore lead to formation of small bubbles of H_2 which could contribute to a poorly adhered copper deposit. The evidence of this was observed by 3-4 μm diameter pits in the nickel surface underneath where the deposit feature had peeled away.

The deposits plated with ultrasound bursts during the off-time however always adhered to the surface. This indicates that the flow from the ultrasonic probe was more successful at replenishing Cu^{2+} ions with the electrode gap from solution outside the gap compared to silent conditions. It was also observed that etched copper from the anode was removed from the gap during the ultrasonic bursts, eliminating restrictions in convection. These would both result in a higher concentration of Cu^{2+} ions within the electrode gap. This increase in ion concentration near the electrode surface may have led to an increase in deposition rate, shown by the 20% increase in deposit thickness in figure 3(d) compared to that in figure 3(c).

4. Conclusions

The effect of US agitation and the use of long current pulses on the electrodeposition of copper patterns in an Enface tank system were investigated. 1 x 5 mm copper features were deposited onto a nickel substrate with a deposit thickness of 4-5 μm and roughness of 1.87 μm and 2.84 μm when plated at 50% i_{Lim} and 75% i_{Lim} under silent conditions. When using long current pulses the deposit roughness was reduced to 0.042 μm and also produced a steadier potential during plating, but the deposits had bad adherence of deposit to the substrate.

Inducing US bursts for 10 seconds during 25 second off-times of the long current pulses produced an even more constant potential wave form, improved the copper deposit adherence and also effectively flushed out etched copper from the electrode gap which was often entrapped between the electrodes during silent plating experiments. It has therefore been demonstrated that using a pulsed US agitation regime can assist electrodeposition by improving both the plating process and properties of the deposited metal.

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