Ultrasonics - Sonochemistry 42 (2018) 445–451

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

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

Design of an ultrasonic tank reactor for copper deposition at electrodes separated by a narrow gap

Simon J. Coleman*, Sudipta Roy

Department of Chemical and Process Engineering, University of Strathclyde, James Weir Building, 75 Montrose Street, Glasgow G1 1XJ, UK

ARTICLE INFO

Keywords:
Copper
Electrodeposition
Ultrasonic
Reactor design
Mass
Transfer
Maskless

ABSTRACT

This work describes the design and testing of an ultrasonic reactor suitable for processes which require agitation within a narrow gap in a tank geometry. A maskless microfabrication process was used to validate the ultrasonic reactor design. This mask-less electrodeposition method requires the inter-electrode distance between the anode tool and the cathode substrate to be maintained at 300 μm, and sufficient stirring of the electrolyte by ultrasound agitation. A design was proposed allowing 74 mm × 105 mm size substrates to be mounted into an electrode holder and loaded into an 18 L ultrasonic reactor. Experiments were carried out to test the uniformity of the mass transfer within the narrow electrode gap at different locations on the substrate, and to validate the feasibility of a mask-less metal plating technique by depositing features of μm-scale. When increasing ultrasonic powers from 30 to 60 W L^{-1}, increasing agitation was observed at the centre of the substrate, but not at its edges. A Sherwood number correlation showed developing turbulence within the narrow gap, even in the centre of the plate. Micron scale features were plated onto A7 substrates, but the deposited features were 2.5 times the original width. The work showed that sonic streaming can produce sufficient agitation in long sub millimetre channels which can be employed to overcome mass transfer limitations.

1. Introduction

Microfabrication is used to construct functional patterns onto surfaces as part of the manufacturing process for a variety of devices, including micro-fluidics, MEMS, micro-optic and micro-electronic systems [1,2]. These devices commonly require through-mask metal deposition [1–4]; the mask typically being fabricated using photolithography [5]. Despite its popularity, photolithography has many disadvantages: (1) it is a complex multi-step process, (2) the process uses hazardous chemicals, (3) which produces a large amount of waste, and (4) requires specialised expensive infrastructure.

A variety of techniques have been proposed to reduce the use of photolithography [6–11]. This includes a variety of additive electrochemical techniques, such as localised electrodeposition [6], electrochemical printing [7], Inkjet techniques [8], and direct writing [9,10]. One such technology is Enface [11], in which, instead of applying a mask to the substrate surface, photolithography is carried out on a tool. The patterned tool is then placed in close proximity (< 500 μm) to the substrate. A current is passed between the two electrodes, thereby selectively etching or plating the desired metal pattern onto the unmasked substrate. Since the tool can be used repeatedly to pattern many substrates, this technique can significantly reduce the use of photolithography.

Previous experimental attempts of this technique have focused on transferring metallic patterns on small-scale substrates of 10 mm diameter [12–15]. Modelling the process suggested an inter-electrode gap of 300 μm was required to transfer metallic features between 5 and 100 μm [16]. The results also showed that forced convection within this narrow inter-electrode gap was necessary to ensure sufficient delivery of fresh solution and removal of by-products. Owing to the importance of agitation in this process, a parallel plate electrochemical flow cell was used to provide forced convection in experiments, which was adapted from an earlier work where electrodes were not in close proximity [17]. That flow system cannot be deployed for larger electrodes due to high pressure drops in channel flow through a narrow gap. Further experimental results showed that natural convection conditions also did not provide sufficient agitation within the inter-electrode gap [14,18]. These natural and forced convection results proved that in order to use the same technique for patterning larger substrates, an appropriate agitation method within the electrode gap was necessary.

Ultrasonic (*US*) agitation has been shown to improve stirring in electrochemical systems [19–21] due to cavitation phenomena [22–24]. Therefore, the authors of this paper carried out experiments to

* Corresponding author.
E-mail address: simon.coleman.sjc@gmail.com (S.J. Coleman).

https://doi.org/10.1016/j.ultsonch.2017.11.038
Received 29 July 2017; Received in revised form 12 November 2017; Accepted 28 November 2017
Available online 02 December 2017

determine if *US* agitation could be used to provide stirring for metallisation using Enface technique [15,25–29]. An initial assessment using an *US* probe placed within a 500 mL 'beaker-type' system was shown to improve mass transfer by ten-fold during copper deposition within an electrode gap of 1500 µm [25]. This suggested that *US* agitation could be a suitable agitation technique for the Enface method. Further copper deposition experiments using 10 mm diameter substrates showed that fluid agitation effectively removed bubbles and etched material from the inter-electrode gap [15,26,27] thereby improving deposit properties [15].

However, it has also been found that employment of an *US* probe can cause potential distortions within an electrochemical cell [25,30] and not useful for scale up purposes. Therefore for larger scale applications, an *US* bath may be a more suitable apparatus. Additionally, more uniform agitation is achieved within the tank of an *US* bath compared to employing an *US* probe [31], which could ensure similar material transport across a large substrate. However, the intensity of the *US* power is generally lower in bath systems than in probe systems [32]. Currently, only limited information is available for *US* applications using a bath [33]. Therefore it is unclear if such an apparatus can be used for providing agitation within a narrow gap.

This work reports the design and testing procedure using a large-scale *US* tank which could provide adequate fluid agitation within a narrow inter-electrode gap. This design would be suitable for reaction systems where mass transfer limitations occurred due to the proximity of reaction surfaces. The design and testing has focused on copper electrodeposition and micro-fabrication by using 74 mm × 105 mm substrates. Copper plating is chosen because it is well known that Cu reduction is characterised by fast kinetics and slow material transport. This reactor design should also be suitable for reaction systems where mass transfer limitations occurs in a narrow gap. The main aims of this work were to: (i) assess mass transfer within a narrow gap between two substrates of 74 mm × 105 mm, which correspond to an A7 size, placed in an 18 L tank; (ii) testing the uniformity of the mass transfer at different locations on the substrate and developing a mass transfer correlation; (iii) and perform mask-less metal plating at the µm-scale as a verification of its usefulness applicability of *US* agitation to.

2. Reactor design

2.1. Electrode holders

At first a design was proposed which would allow A7 size substrates to be mounted into the electrode holder and loaded into the reactor. The design had to consider that the plates had to be contacted to the power supply (but sealed against any electrolyte ingress to avoid shorting), and be dismounted after deposition, washed and extracted from the holder without touching the deposit or the substrate surface.

Fig. 1 shows the electrode holders used in the deposition experiments. The holders were fabricated from two PVC blocks and were designed to hold two A7 size electrode plates. The electrodes were made from high conductivity oxygen-free copper plates (*Advent*). The holders were screwed together with plastic bolts so the plates face each other with an electrode gap between them. The electrical connection was made from the back of the plate. When the holders were screwed together, the plate was pressed tightly against a copper block at the back of the holder. A copper rod was screwed into the top of the block to which electrical contacts were connected. Electrical insulation covered the area of the copper rod that was submerged in the electrolyte to prevent any electrical contact with the electrolyte solution. A Perspex rod was also screwed into the holder for extra support. These rods were then screwed into a support block above so the holders could be suspended in the solution, as shown in Fig. 2.

In order to ensure that the inter-electrode gap was accurate, spacers made from PTFE sheet were placed in the corners and middle of the plate. For the mass transfer experiments, a gap of 1.5 mm was used. This allowed the authors to compare data obtained for the A7 substrates with those obtained for smaller ones [25]. An electrode gap of 0.3 mm, or 300 µm, was used for the micro-scale pattern deposition. The accuracy and variation in the inter-electrode gap was measured by applying silicone sealant at various locations on the copper plate. The spacers were placed into position and the holders were screwed together. The silicone was then left to dry, after which the holders were unscrewed and taken apart. An optical microscope was then used to measure the thickness of the dried silicone sealant at different locations on the plate. These measurements showed that there was a variation of ± 40 µm across the plate. This variation arose due to the natural curvature of the metal substrate and therefore could not be eliminated.

2.2. Electrodes and tools

Mass transfer experiments were carried out in the *US* tank by using a tool such as shown in Fig. 3(a) to measure the limiting current at two different locations. This tool was a 1 mm thick Perspex sheet with 10 mm × 10 mm square holes, into which 10 mm × 10 mm polished copper squares could be slotted. This tool was placed into the electrode holder with a copper foil placed behind it which allowed for electrical connection from the back. The slotted copper squares then served as anodes for experimentation. An A7 copper plate, placed in the opposite holder, served as the cathode. Either of the squares, A or B, could be connected up individually to the electrical connection. This made it possible to measure the limiting current at the corner and near in the middle of the plate separately. These locations were important, since one site is more accessible for ionic species; a comparison of mass transfer conditions would allow one to estimate the differences in material transport at the two positions. In particular, A is located at the centre, just above the spacer which could impede mass transfer.

Micron scale features were electrodeposited using a specialised anode (which is referred to as tool) and cathode. Both the anode and cathode were made from high conductivity oxygen-free copper plates (*Advent*), cut into A7 size rectangles. The substrates were washed thoroughly with diluted Decon 90 solution and polished manually with #1200, #2400 and #4000 grit SiC paper. They were then rinsed with deionized water and dried thoroughly using a nitrogen gun. The anode was then masked by E9230 dry resist with µm-scale linear features (210 µm width lines of exposed copper surface, with 1040 µm width lines of resist between each exposed copper line), such as that shown in Fig. 4(a). Linear features were chosen to evaluate if *US* agitation: (1) caused photoresist delamination during electrodeposition, and (2) if there was significant differences in replication of pattern at different locations of the tool. The protocol for the fabrication of this tool is described elsewhere [34].

2.3. The tank

US agitation was provided by a *Hilsonic US* tank with a capacity of 18 L, which is the smallest size used in industrial plating applications. Since the system was to be used for electrodeposition of copper from an acid bath containing chloride ions, a hard enamel coating was applied to the walls to prevent the steel walls coming into electrical contact with the electrolyte solution. Fig. 2 shows the location of the transducers on the walls of the tank, with 5 transducers on each side-wall and 4 on the bottom. The transducers operated at a frequency of 30 ± 2 kHz and three different powers, 30, 40 and 60 W L^{-1}, were used in the experiments. Although these powers would normally produce sufficient agitation within the tank, the stirring within a narrow gap is severely restricted due to the limited penetration of flow of ultrasonic streaming, which needs investigation. In each experiment, the electrode holder was immersed into the *US* tank and placed into the position so that the locations of the transducers are situated side-on to the electrodes. The electrodes had to be positioned at distances further than 30 mm from the walls of the tank, in order to obtain an even *US* agitation. The *US*