Electrodeposition of Microstructures using a Patterned Anode

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Abstract

In this paper we report the transfer of micro-scale patterns by electrodeposition on to substrates without requiring them to be coated with a photoresist mask. This approach makes uses of a patterned tool which is placed in close proximity to the substrate in an electrochemical reactor. With an appropriate choice of electrochemical parameters, electrodeposition can be confined to regions corresponding to the exposed regions of the tool. Experiments indicate that the electrodeposition of copper features on to conductive substrates is possible using this approach. Copper lines of 100 μm width have been successfully replicated, but with some increase in dimension due to current spreading. This effect can be minimised by reducing the inter-electrode gap and employing an electrolyte with a low conductivity. It is also demonstrated that the tool can be used to pattern multiple substrates.

Keywords: electrodeposition, etching, microfabrication, copper.

1. Introduction

Electrochemical microfabrication techniques are routinely used in the manufacture of microsystem devices [1]. Broadly, these techniques can be classified as 'additive' methods were electrodeposition is used to deposit material on to a substrate or 'subtractive' where electrochemical etching is used to remove material. Additive processes are usually based on the technique of 'through-mask' plating [2] while subtractive ones typically employ masked electrochemical etching [3]. In both of these approaches the substrate is patterned with a photoresist material which acts as a mask to define the areas to be etched or plated. More recently, techniques based on patterned electrodeposition using conformal masks have been developed [4,5].

A wide range of other electrochemical techniques (including mask-less and direct-write processes) have also been developed to deposit micro- and nano-structures on metal and semiconductors substrates [6-11]. Often these involve rastering a sharp electrode tool over the substrate, or using light or other forms of radiation to induce localised deposition [6-8]. Meniscus-confined electrodeposition of 3D microstructures has also been demonstrated [9]. These techniques are capable of high spatial resolution and accuracy, but many [6-9] are essentially serial fabrication methods are generally not suitable for volume production of micro-devices.

Roy [12-15] has recently proposed an alternative electrochemical microfabrication technique known as 'EnFACE' which can be used to etch micro-patterns on copper

substrates. They used a tool patterned with a photoresist mask while the substrate remained fully exposed. The tool and substrate were mounted in opposite walls of a flow channel. By employing a very small gap (< 500 μm) and a suitable electrolyte, selective metal dissolution on the regions facing the exposed portions of the tool were achieved. In this manner, micro-scale patterns which were considerably smaller (i.e. 50 – 200 μm) than the electrode gap were transferred to the substrates.

This technique has the advantage that a single patterned cathode can be used to etch many substrates. This is contrast to conventional etching techniques where each anode substrate has to be individually patterned with a photoresist mask [3]. By minimising the demands for lithography, this technique has the potential of drastically reducing the cost of electrochemically micro-fabricated parts. It is also a parallel microfabrication method with corresponding advantages in cost and throughput. While EnFACE was originally developed for etching, patterned electrodeposition is also feasible.

The objective of this paper is to report the results of pattern transfer achieved by electrodeposition. In this study we report for the first time the electrodeposition of copper on to substrates using the EnFACE process and the electrochemical parameters required for good pattern transfer.

2. Experimental

The apparatus used in the present study is similar to that used in the etching experiments and is described in detail in earlier publications [12,13]. It is shown

schematically in Figure 1, which indicates the relative disposition of the anode tool and cathode substrate and other key components. The anodes were fabricated from 1 cm diameter polished copper disks (99.99%). These were patterned with a 7 μm thick layer of SPR 220 resist (Rohm & Haas) using standard photolithographic techniques. This exposed a series of parallel 100 μm wide exposed copper lines separated by 500 μm lines of photoresist. The electrochemically active area of the anode was therefore 16% of the total area. The cathode substrates were 0.9 and 1.2 cm diameter polished nickel disks (99.99%). Deposition of copper on to the nickel electrode by a displacement reaction was restricted to a thickness < 10 nm and can therefore be neglected.

The anodes and cathodes were mounted in PTFE cups so that only their front faces were exposed to the solution. These were inserted into electrode holder plates which were then fixed on either side of the flow channel reactor. When assembled, the electrodes face each other with a nominal inter-electrode gap of $h = 250$ μm. The uncertainty in the gap distance is estimated to be ± 25 μm. However, the electrode was deliberately recessed into its holder to improve current uniformity, so that the minimum inter-electrode spacing was 300 μm.

The electrolyte solution used in these experiments comprised 0.1 M $CuSO_4$. During the experiment the electrolyte was circulated through the flow channel using a flow rate of 40 ml s^{-1}. Electrodeposition experiments were carried out galvanostatically using a DC power supply or a pulse rectifier. In all experiments reported here the current density is defined relative to the exposed area of the anode. Optical inspection and the measurement of line-widths on the plated samples were performed with an

Olympus MX-50 microscope equipped with a dimensional measurement system. The deposit thickness and roughness was measured using a stylus profilometer (Dektak 6M, Veeco).

3. Results and Discussion:

3.1 Limiting Current Measurements

Initially experiments were performed on un-patterned copper substrates to determine the limiting current for copper deposition in a 0.1 M $CuSO_4$ with different electrode spacings. This is an important parameter to establish because, if exceeded, the deposit morphology and current efficiency can be adversely affected. As expected, the limiting current decreased as the recess depth increased [16]. At a flow rate of 40 ml s^{-1} the limiting current at spacings of 300, 500, 750 and 1000 μm were 78, 68, 58 and 44.5 mA cm^{-2}, respectively. A gap of 300 μm was used for all subsequent experiments, since the previous etch trials [12,15] had indicated that narrower gaps improved pattern definition.

3.2 DC Plating Experiments

Initial DC plating experiments were performed in 0.1 M $CuSO_4$ under the conditions described in Table 1. The current densities were chosen to be 30% - 120% of the limiting current and the deposition time was fixed at 30 seconds. These conditions resulted in good replication of the linear pattern on the cathode substrate (Figure 2a, b) but there was some broadening of the copper lines due to the current spreading effect (Table 1). Below the limiting current, the dependence of linewidth on current density was difficult to quantify, but the narrowest line (120 μm) was obtained at current

density of 46 mA cm^{-2}. This showed that the current spread could be limited to 20%. At the highest current density (120% of limiting current) the width of the plated copper lines was 250 μm. Previous studies [15] have shown that a predominantly primary current distribution will minimise current spreading. This suggests that low solution conductivity, a small electrode gap and high current density should lead to optimum pattern transfer.

Linewidths were also found to depend on their radial location on the substrate. Lines were generally narrower at the centre but became wider near the edge of the substrate. This could reflect the current distribution at different radial locations of the electrode, especially near the edge. Another issue was that the polished surfaces were slightly convex so that the electrode separation was ca. 50 μm larger at the edges than at the centre [12,15]. As current spreading is dependent on the inter-electrode gap, this could also contribute to variations in linewidth over the surface.

Deposit morphology and appearance of the DC plated copper lines is summarised in Figure 2. Figure 2a shows that copper lines exhibit a metallic appearance consistent with a low surface roughness, as would be expected when it is deposited below the limiting current. In contrast Figure 2b shows dull, 'burnt' copper lines indicative of higher surface roughness, as would be expected when they are plated at higher than the limiting current. The thickness and width of copper lines deposited at 46 mA cm^{-2} for different times is shown in Figure 3a. The roughness increases substantially with thickness but such roughness evolution is typical for copper plating from electrolytes which do not contain additives.

Figure 3b indicates that the thickness increases linearly as a function of time. Note that the data point at 60 seconds appears slightly anomalous but this reduced height reflects the broadening of this line relative to the others (Figure 3a). The deposition rate calculated from the slope of the regression line is approximately 1.2 μm min^{-1} based upon measurements near the centre of the cathode. This is close to the expected deposition rate (1.1 μm min^{-1}) based on the nominal current density defined at the anode and assuming 100% current efficiency and negligible current spreading.

3.3 Pulse Plating Experiments

Since pulse plating can produce a more primary current distribution than under equivalent DC conditions [17] deposition was also performed by current pulsing. Current on/off times of 10/50 ms were used corresponding to a duty cycle of $\theta = 0.17$. The peak current density was set at 276 mA cm^{-2} in order to maintain an average current density of 46 mA cm^{-2}. Deposits plated by pulse currents from a 0.1 M $CuSO_4$ solution are shown in Figure 2c and the results are summarised in Table 1. The deposited lines were found to be sharp in most cases with a relatively low surface roughness. The line thickness in one experiment is restricted to 150 μm even when the deposit thickness was 2.6 μm. These preliminary results did not indicate a significant reduction in current spreading compared to DC, but did appear to suppress the evolution of roughness at high deposit thicknesses.

3.4 Tool Requirements

Since the EnFACE technique requires a re-usable tool, it is important to verify that the tool does not deteriorate during the pattern transfer experiments. Inspection of the anodes used to plate multiple substrates revealed that they had been etched to a depth

of tens of microns in the exposed areas without affecting the resist mask. Although it is undercut (Figure 2d) the insulating surface remained intact and the current distribution will not be significantly changed. The use of an insoluble anode system is also feasible, although it is possible that a gas evolving anode reaction could lead to gas entrapment in the electrode gap. In this case, an alternative anode system would be the oxidation of ferrous to ferric ions, which is routinely used for copper plating of printed circuit boards [18].

3. Conclusions

The electrodeposition of micron-scale copper features on to fully exposed substrate using a masked tool has been demonstrated. Linewidths of 120 – 200 μm have been successfully reproduced on the substrate with a total deposit thickness of up to 2.5 μm. Some broadening of the lines occurs due to current spreading effects, but these can be minimised by using a small inter-electrode gap and an electrolyte with a low conductivity. The tool was re-used to pattern multiple copper substrates without significant deterioration. Further research is currently underway to examine the reproducibility and scalability of the process and examine the deposition of other metals.

Acknowledgements

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Deposition Mode	Average Current Density (mA cm^{-2})	% DC Limiting Current	Deposition time (s)	Minimum linewidth (µm)	Thickness (µm)	Deposit Appearance
DC	23	30	30	150	0.4	Sharp, bright lines
DC	46	60	30	120	0.6	Sharp, bright lines
DC	69	90	30	150	0.8	Sharp, bright lines
DC	92	120	30	210	1.0	Broad, dull lines
Pulse 10/50	46	60	60	200	0.75	Broad lines
Pulse 10/50	46	60	120	150	1.3	Sharp lines
Pulse 10/50	46	60	240	150	2.6	Sharp lines

Table 1: Summary of results from DC and pulse plating experiments in 0.1 M $CuSO_4$.

Figure Captions:

Figure 1: Conceptual illustration of micro-scale deposition on to a cathode using a patterned anode. Arrows indicate the spreading current lines emerging from the anode. a indicates the mask dimension, b is the plated linewidth and h is the inter-electrode gap.

Figure 2: Images of plated cathodes and etched anodes. (a) cathode - DC plating at 46 mA cm^{-2} for 30 seconds (b) cathode - DC plating at 92 mA cm^{-2} for 30 seconds (c) cathode - pulse plating with 10/50 ms pulses for 60 seconds (d) anode tool after multiple deposition experiments. White scale bar at bottom left corner indicates a width of 200 μm.

Figure 3: (a) Profilometer scans showing the thickness, roughness and width of plated copper lines obtained at 46 mA cm^{-2} for various plating times. (b) insert graph shows thickness as a function of time.

Figure 1:

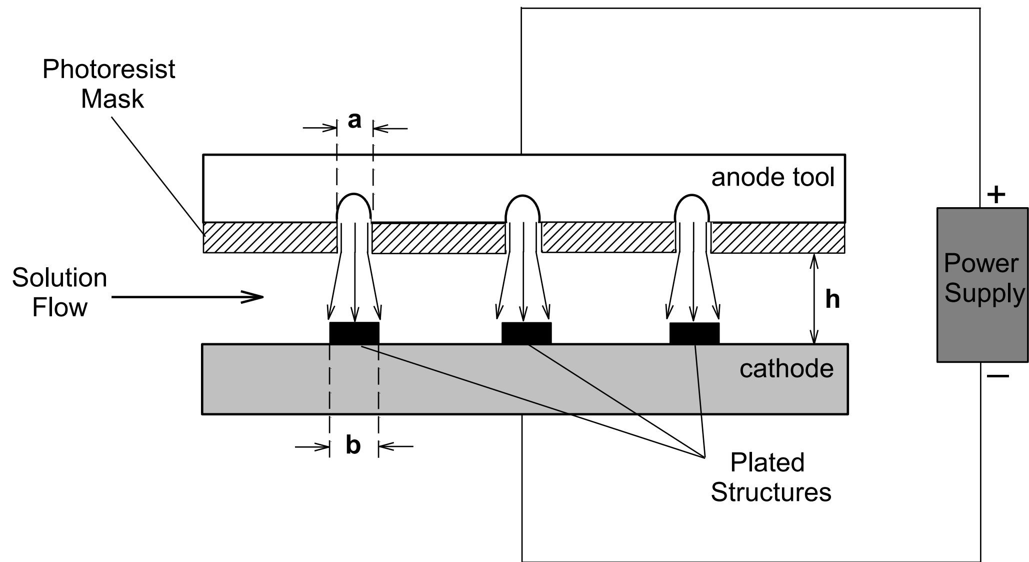
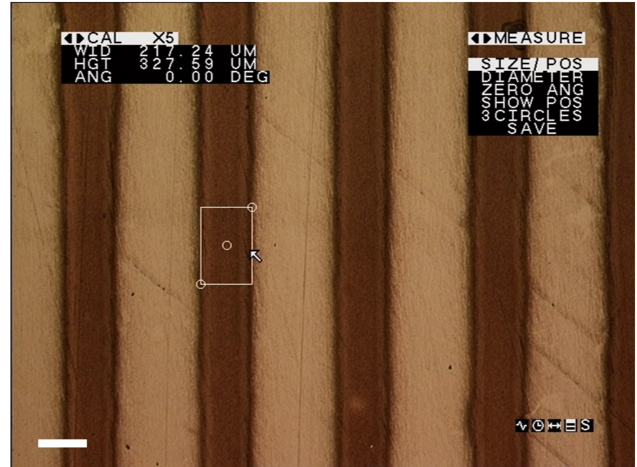
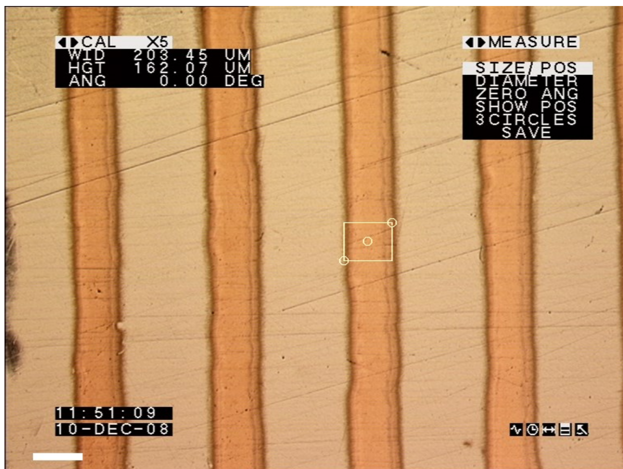


Figure 2:

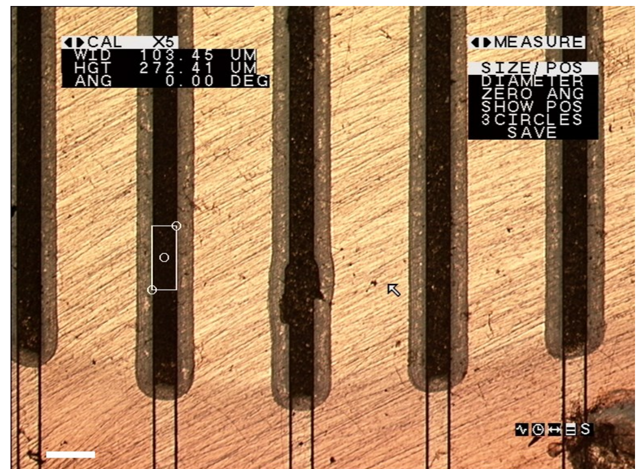
(a)



(b)



(c)



(d)

Figure 3: