

# Sono-electrodeposition transfer of micrometric Copper patterns on to large substrates

Albert Serrà <sup>a</sup>, Simon J. Coleman <sup>b</sup>, Elvira Gómez <sup>b</sup>, Todd A. Green <sup>b</sup>, Elisa Vallés <sup>a</sup>,  
Joan Vilana <sup>a</sup>, Sudipta Roy <sup>b</sup>

<sup>a</sup> *Grup d'Electrodeposició de Capes Primes i Nanostructures (GE-CPN), Departament de Química Física and Institut de Nanociència i Nanotecnologia (IN<sup>2</sup>UB), Universitat de Barcelona, Martí i Franquès 1, E-08028, Barcelona, Spain.*

<sup>b</sup> *School of Chemical Engineering and Advanced Materials (CEAM), Merz Court, Newcastle University, Newcastle upon Tyne NE2 7RU, UK.*

## Abstract

The Electrochemical nano-Fabrication using Chemistry and Engineering (*EnFACE*) technology has been demonstrated as a successful method to transfer centimetre and micrometric copper patterns onto flat pieces of several centimetres in wide (A7 size plate) in a narrow electrode-gap configuration. A non-acidic copper (II) bath with a low content of additives has been used. The copper transfer from the photolithographed anode to the flat polished cathode with high efficiency has been possible maintaining very narrow separation between the two electrodes (300  $\mu\text{m}$ ) and controlled ultrasonic stirring (US) (sono-electrodeposition transfer) during galvanostatic process. By using the designed tank and electrode configuration, both centimetre squares and micrometric lines features of micrometric thickness has been transferred in different points of the centimetre cathode, with better definition using low ultrasound power (enough forced convection flow to attain the needed transport to and from the electrode surface) in different zones of A7 plate. Excessive mass transport enhancement promoted a poor definition due to the current spreading during the deposition. In order to obtain micrometric features, a previous immersion in surfactant solution before plating favours the wettability of the electrodes and the uniformity of the lines after the transference.

The proposed approach for plating of micrometric features to obtain patterned substrates is a good alternative to the classical electrodeposition process in photolithographed substrates. Similar definition is obtained in the both procedures, but the sono-electrodeposition provides the possibility to re-use the electrochemical tool up to fifth times, by maintaining the efficiency and uniformity of the transfer, which shows a significant gain in the efficiency of the microfabrication process in contrast with conventional techniques where each anode or cathode substrates have to be patterned individually with a photoresist mask for once. The presence of chloride in the solution inhibits the anode passivation, even in a non-acidic medium. Therefore, the improvements to use a low ultrasonic power and a non-acidic bath with additives in comparison with high ultrasonic power and acidic bath are the lower surface roughness, less current spreading and prolonged life of anode tool.

## **1. Introduction**

Copper electrodeposition has been a burgeoning topic and an important key for a long time due to its interest in the fabrication of many micro and nanodevices as a consequence of its wide range of applications, highlighting the massive use in the electronic [1-2], optoelectronic [3], microfluidics [4] and microelectromechanical systems (MEMS) [5-6] industries.

Electrochemical methods permit an easy control of growth processes, chemical composition, and crystalline structure when micro and nanostructured materials are prepared [7-8]. In recent years, many strategies using soft-templates like microemulsions [9-10], assembly of micelles [11], self-assembled monolayers [12], amongst others, have been proposed as required complement for the electrochemical nanofabrication of nanowires, nanorods, nanoparticle or other nanostructures, avoiding the use of the classical hard templating [13-15]. However, scalable and forthcoming micro and nanofabrication technologies, including the classical electrochemical procedures, require methods of patterning substrates, especially hard-templating strategies, in order to define the desired micro or nanostructure [16-17]. In this way, photolithography has been an essential step for microfabrication [18-19], but it requires physical master masks and mainly inflexible substrates, limiting the use of non-rigid substrates, multiple alignment, and 3D fabrication, amongst others [20-23]. Therefore, the development of alternative technologies, avoiding the substrates patterning with a physical mask, is suitable for these applications in order to improve the efficiency, develop environmentally friendly processes and reduce costs.

Nowadays, Electrochemical nano Fabrication using Chemistry and Engineering (*EnFACE*) technology (c.f. Figure 1) explore the possibility to do an electrochemical selective and localized deposition or etching on an unmasked substrate, using a pattern masked counter-electrode, as an electrochemical tool [24-27]. The main advantage of this technique, which does not avoid the use of a physical mask, is that a single patterned cathode or anode could be used to etch or electrodeposit, respectively, many times, showing an interesting gain in the efficiency of the microfabrication process in contrast with conventional techniques where each anode or cathode substrates have to be patterned individually with a photoresist mask for once [24-27]. However, this technology requires control the reactor design, especially the required inter-electrode gap of less than 500  $\mu\text{m}$ , the flow conditions in order to improve mass transport, and the electrochemistry of the system to achieve a good microstructure definition. Therefore, the mass transport and the bubble retention within the narrow electrode gap during the process, especially in the case of deposition, could be a limiting drawback, which disable the potentiality of this proposal. Ultrasonic (US) stirring is also known as a good strategy to improve the stirring in the electrochemical systems [28-29]. Moreover, accordingly with previous studies, the US agitation improves significantly the mass transfer within a narrow electrode gap during the cooper deposition [26-27]. However, high US powers could improve the mass transport, but limiting the life time of the patterned electrochemical tool. Furthermore, the chemistry of the selected system could affect drastically the definition of the shape and the size of the transferred pattern, especially by the passivation dynamics of the electrochemical tool [24] when non-acid bath was used and the cooper was oxidized to copper oxides.

**Figure 1:** Schematic diagram of EnFACE patterning process versus conventional methodology. **Todd version.**

Recently, it was demonstrated that the electrodeposition of patterned cooper onto A7 cooper plates (width: 74 mm and height: 105mm) using EnFACE technology at high ultrasonic power is possible [SS], exhibiting the viability to scale this procedure. However, high ultrasonic powers reducing the life of electrode tool, as

a consequence of the anode damaging, and lead to poor definition (high current spreading) and excessive rougher surfaces. Herein, we propose the electrodeposition of patterned copper onto A7 copper plates at low ultrasonic power, in order to analyse the effect on the pattern definition and the life time of the electrochemical tool. A non-acidic bath with a low content of additives is used, in order to analyse the decrease of the solution conductivity, poor wetting, the passivation effect of the electrochemical tool and the effects of additives in the microstructure, especially in terms of surface roughness, and shape and size of the transferred pattern.

## 2. Experimental

### 2.1. Bath composition:

Non-acidic bath with commercial additives, which are normally used to plate printed circuits boards (Copper Gleam HS 200 – Dow Electronic Materials), was selected in order to improve the electro-transfer parameters. Therefore, the electrolyte solution was a free-acid copper bath of  $0.1 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O} + 5 \text{ mL} \cdot \text{L}^{-1}$  of Gleam HS-200B (carrier/suppressor) +  $2.5 \text{ mL} \cdot \text{L}^{-1}$  of Gleam HS-200A (brightener/accelerator) +  $35 \mu\text{L} \cdot \text{L}^{-1}$  of HCl. The electrolyte solution was prepared with deionized water with a resistivity of  $13.7 \text{ M}\Omega \cdot \text{cm}$ . It is important to note that the recommended additives concentrations are  $10 \text{ mL} \cdot \text{L}^{-1}$  of Gleam HS-200B, +  $0.5 \text{ mL} \cdot \text{L}^{-1}$  of Gleam HS-200A and  $163 \mu\text{L} \cdot \text{L}^{-1}$  of HCl, and besides, normally this process contains sulphuric acid. However, the selected conditions are justified in order to reduce surface roughness and to promote the electro-transfer.

### 2.2. Experimental set-up:

Electrochemical experiments were carried out in an 18 L ultrasonic tank reactor connected to three ultrasonic generators (Hilsonic) with a PVC electrode holder (**Figure 2**). Calorimetric method were used for measuring and calibrating the ultrasonic power using water [30-31]. Cathode and anode were A7 copper plates (width: 74 mm; height: 105 mm; and thickness: 1.1 mm). The gap distance between the electrodes and the electrode preparation vary depending on the experiment:

- **Limiting current experiments:** Inter-electrode gap of 1.5 mm. Anode: Each copper square (10 mm x 10 mm) was manually polished with #1200, #2000 and #4000 grit SiC paper, washed with Decon 90 solution, rinsed with deionised water and dried thoroughly using nitrogen. Then, they were pushed into the Perspex sheet (**Figure 1S**). Each limiting current experiment was repeated three times and

carried out individually in different positions (the other squares were masked with spray resist and blockaded with a polymeric layer on the back in order to assure the non-electrical connection. Cathode: A7 copper plates polished and cleaned in the same way.

- **Pattern electrodeposition experiments:** Inter-electrode gap of 0.3 mm. Electrodes: Each A7 copper plates were manually polished, washed, rinsed and dried in the same way. Anode: Square (10 mm x 10 mm) and linear (width: 210  $\mu\text{m}$ ; height: 78  $\mu\text{m}$ ; photoresist spacing between the lines: 1000  $\mu\text{m}$ ) pattern features were deposited using spray resist tool fabrication (**Figure 2S**) and dry photoresist tool (**Figure 3S**), respectively. As can be seen in Figure 2Sb the spray resist tool preparation consisted in the following steps: (i) mask areas with 1 x 1 cm squares of copper tape; (ii) spray photoresist over the entire surface, and dry using an air dryer during 10 minutes; (iii) remove copper squares from the plate; (iv) back in oven at 50 °C for 20 minutes; and lastly, rinse with deionized water and dry thoroughly with a nitrogen gun. Figure 3S shows the dry photoresist tool **Photoresist preparation procedure ? To do, could you complete this part?**

All the electrochemical experiments were carried out using a power supply (Thurlby Thandar PL320) under DC conditions.

**Figure 2:** Side view of the experimental 18 L ultrasonic tank.

### **2.3. Surface characterization:**

Confocal microscope was used to achieve a precise control of the definition along the large area of an A7 copper plate. A 3D Optical surface metrology system Leica DCM 3D was used to determine the thickness and roughness of the transferred patterns.

### 3. Results and discussion

#### 3.1. Limiting current experiments:

It has been known that high ultrasonic irradiation on electrodeposition leads to both chemical and physical effects (mass transport enhancement, surface cleaning, amongst others) [32-33]. Herein, the sono-electrodeposition at low power in a free-acid copper bath was investigated in order to establish the ultrasound effects on the mass transport, by limiting current measurements, in a parallel plate electrodes configuration with a narrow electrode-gap. The experimental configuration requires the evaluation of mass transport in different zones (I and II, schematically illustrated in Figure 1S). Typically, limiting current densities ( $j_{lim}$ ) were obtained directly from the plateau region in applied current densities ( $j$ ) versus potential ( $E$ ) curves. The limiting current experiments were carried out by applying current densities ( $j$ ) between 10 to 120 mA·cm<sup>-2</sup> for 30 seconds and measuring the cell potential ( $V$ ) as a consequence of the experimental set-up. The limiting current region could be affected by several factors such as the secondary reaction (hydrogen evolution), variations in area during the metal deposition, current and potential distributions, amongst others. Recently, significant distortions in the polarisation data have been observed at narrow electrode-gap distance in parallel electrode plate configuration [34]. As can be seen in Figure 3 the significant slope in the limiting current region could affect the measurements. However, the direct determination from the pseudo-plateau region was coherent according to the limitations of the experimental configuration. **Table 1** shows the limiting current densities at different low power, showing an enhancement in the limiting current density by increasing the ultrasound power as can be expected according to the literature [34-36]. Furthermore, the diffusion layer thickness ( $\delta$ ) that could be calculated using limiting current from eq. (1) is frequently used in order to characterize the mass transport conditions (Table 1).

$$\delta = \frac{z \cdot F \cdot D \cdot c_b}{j_{lim}} \quad Eq. (1)$$

Where  $z$  is the charge on the reacting species,  $F$  is the Faraday constant (96485 C·mol<sup>-1</sup>),  $D$  is the diffusion coefficient of the electroactive species, assuming the calculated value of 7.07·10<sup>-6</sup> cm<sup>2</sup>·s<sup>-1</sup> [36], and  $c_b$  is the concentration of the reactant ions in the bulk solution.

As can be seen in Table 1 the ultrasonic power lead to increase the limiting current and decrease the diffusion layer thickness, which can be attributed to the cavitation and/or micro and macro-streaming effects. Non-significant differences could be observed in the different zones (I and II) of the electrode. Therefore, low ultrasound power could be feasible as a forced convection flow to attain the needed transport to and from the electrode surface, even in the centre part (part II) of an A7 plate in a narrow electrode-gap configuration. Furthermore, the limiting current experiments were a fundamental step in order to choose the current for the pattern transfer deposition. Moreover, it is important to note that the limiting current experiments were carried out using an inter-gap distance of 1.5 mm instead 0.3 mm that we use to transfer the patterns. Therefore, 20 and 30 mA·cm<sup>-2</sup> must be feasible to do the sono-electrodeposition transfer because limiting current at 0.3 mm must be lower than at 1.5 mm, and it is important that the limiting current does not exceeded because the deposits will become dendritic and roughness will increase drastically.

**Figure 3:** Limiting current experiments under direct current (DC) conditions at different ultrasonic powers at the (a) corner (position I) and (b) the centre (position II) of the A7 plate.

Power / W·L <sup>-1</sup>	Limiting Current / mA·cm <sup>-2</sup>		Diffusion Layer / µm	
	I	II	I	II
5	40	45	34	30
10	50	50	27	27
30	70	70	20	20

**Table 1:** Limiting current, diffusion layer thickness and mass transport coefficients values at different ultrasonic powers at the corner (position I) and the centre (position II) of the A7 plate.

### 3.2. Sono-electrodeposition transfer of centimetre and micrometre features.

The sono-electrodeposition of micrometre lines and centimetre squares were carried out under DC conditions in order to analyse the viability of EnFACE methodology to scale the transfer process. Moreover, the ultrasound power and non-acidic bath with low additive contents effects on the electrochemical tool

and transferred features (electro-transfer efficiency – shape definition and thickness - and surface roughness) was analysed. Therefore, a detailed analysis of the surface roughness of A7 substrates (after manual polishing) was also important. As can be seen in Figure 4 the copper substrates showing highly granular structure with an average surface roughness amplitudes of 160 nm ( $R_a$ ) and of 216 nm ( $S_a$ ), which  $S_a$  corresponds to a 3D amplitude parameter equivalent to the  $R_a$  of a 2D profile [ZZ], with 25  $\mu\text{m}$  and 50  $\mu\text{m}$  Gaussian robust filters, respectively.

**Figure 4:** Representative (a) 3D and (b) 2D profiles of manually polished copper substrates.

### 3.2.1. Sono-electrodeposition transfer of square pattern features:

Various low ultrasonic powers and fixed current density of  $20 \text{ mA}\cdot\text{cm}^{-2}$  (deposition times: 600 s) under DC conditions were used to transfer centimetre square pattern, with squares of 10 mm x 10 mm, located in the corners and in the middle parts of the A7 plates (schematically illustrated in **Figure 3S**), using a spray resist tool. Accordingly, the mass transport enhancement effect on the profile definition and microstructure could be analysed. **Figure 5a** and **4S** show the A7 plates with the electrodeposited square features at different low powers. As can be seen in Figure 4S better features definition has been attained at low power, compared with a poor definition in the case of  $30 \text{ W}\cdot\text{L}^{-1}$ . Moreover, the electro-transfer efficiency of the pattern transfer in the sono-electrodeposition process (**Table 2**) shows that the efficiency ( $\epsilon$ ) increases inversely proportionally to the increase of US power. Therefore, the mass transport enhancement attributed to the increase of US power promoted a poor definition due to the current spreading during the deposition and the corresponding decreasing in the effective current density as a consequence of the increase of effective area. Therefore, better definition and large patten electro-transfer efficiency were attained by applying low power. Moreover, Figure 4S (optical micrographs) also shows that all the ultrasound power led to a closely-packed copper grain structure.

**Figure 5b** show that the average thicknesses of the deposits were approximately 2.6 - 4.4  $\mu\text{m}$  (Table 2), resulting electro-transfer efficiencies of 54 to 90 %. It is important to note that we could define two different



efficiency parameters: current ( $\epsilon$ ) and electro-transfer ( $\epsilon'$ ) efficiencies, which combines both transfer and the electrochemical efficiencies. Current efficiency assume the real dimensions of the pattern area ( $A_f$ ) and electro-transfer efficiencies assume that the dimensions ( $A_a$ ) of the feature are the same as the tool (i.e. that there is no current spreading).

$$\epsilon = \frac{\text{Experimental Average Thickness}}{\text{Expected Thickness}} = \frac{(\text{Experimental Average Thickness}) \cdot n \cdot F \cdot \rho \cdot A_f}{I \cdot t \cdot M}$$

$$\epsilon' = \frac{\text{Experimental Average Thickness}}{\text{Expected Thickness}} = \frac{(\text{Experimental Average Thickness}) \cdot n \cdot F \cdot \rho \cdot A_a}{I \cdot t \cdot M}$$

Where  $n$  is the total number of electrons,  $F$  is the Faraday constant,  $\rho$  is the copper density,  $A_f$  is the real dimension of the pattern area,  $A_a$  is the dimension of the area in the tool,  $I$  the current,  $t$  the electro-transfer time and  $M$  is the molecular weight of copper.

Table 2 also shows that the deposited squares at the edges were thicker, in any US power, than those transferred in the middle due to the different current distribution across the plate. However, it is difficult to analyse these differences in thickness individually due to the large variation in thickness. As can be seen this sense was observed at all the various different ultrasound power that we tested, showing that the different current distribution was the main effect in the thickness definition.

As can be seen in **Figure 5c** the average surface roughness ( $R_a$ ) showing slightly rougher deposits at the corners, at any US power, as could be predicted accordingly to the thickness measures, possibly as a consequence of the higher current densities near the edges of the plate (Table 2). In addition, average surface roughness at different US power (Table 2) decrease when the US power increases. A previous study with no additives bath and higher powers showing that roughness decreasing with increases ultrasonic power [SS]. It is difficult assume that this trend could be explained as a consequence of the current spreading during the deposition, which resulting with a lower current density and higher effective area, because in all the cases the limiting current does not exceed. A more likely explanation is that there is more current spreading at higher US powers so that features are shorter but wider. At higher powers you might also be physically eroding deposited copper from surface or damaging mask.

Lastly, it seems that the chloride inhibits the anode passivation during the sono-electrodeposition providing the possibility to re-use the electrochemical tool several times even in a non-acidic bath. Therefore, non-acidic bath with low content of additives leads to the possibility to do a sono-electrodeposition transfer,

better at low power, of centimetre features with an acceptable thickness homogeneity and good uniformity in the average surface roughness across the plate, even in the central zone.

Power $W \cdot L^{-1}$	Average deposit thickness / $\mu m$			Average Roughness / nm			$\epsilon$ / %	$\epsilon'$ / %
	Corners	Middle	All areas	Corners	Middle	All areas		
5	4.6	4.2	4.4	220	140	180	94	90
10	3.8	3.2	3.5	200	190	195	87	72
30	2.8	2.4	2.6	140	120	130	85	54

**Table 2:** Thickness, roughness and electro-transfer efficiencies of copper electro-transferred centimetre square features at different locations on an A7 plate substrate using various US powers.

**Figure 5:** (a) Optical micrograph of an example of square pattern electro-transfer. (b) Average thickness and (c) average surface roughness amplitude ( $R_a$ ) of copper electro-transfer of square features at various locations on an A7 copper plate prepared at  $20 \text{ mA} \cdot \text{cm}^{-2}$  with a total current on-time of 600 seconds, under DC conditions, at various ultrasound power.

### 3.2.2. Sono-electrodeposition transfer of linear pattern features:

Micrometre linear features were also electro-transferred onto A7 copper plates using a dry photoresist tool under DC conditions at both  $20$  and  $30 \text{ mA} \cdot \text{cm}^{-2}$  and  $5 \text{ W} \cdot \text{L}^{-1}$ . All the electrochemical tools were immersed in a  $0.5 \text{ wt. \%}$  SDS solution before every plate in order to improve the wettability. The SDS was to improve wettability – i.e. allow solution to penetrate fine photoresist features on the tool. US power was selected at  $5 \text{ W} \cdot \text{L}^{-1}$  according to the centimetre square electro-transfer, which as seen previously presents a good shape definition and higher electro-transfer efficiency. Moreover, in order to demonstrate the growth rate effect in thickness and roughness two different current densities were used. The analysis of the electrochemical tool after several uses as a cathode were also analysed in order to determine the possibility to use one tool several times (the main advantage of this methodology). Lastly, direct electrodeposition (classical methodology) using the photolithographed template was carried out in order to demonstrate that EnFACE methodology could be a forthcoming strategy to fabricating micrometre patterns, even using

larges and non-perfectly flatten substrates, with comparable results in terms of shape definition and average surface roughness.

**Figure 6** show examples of the linear pattern that were electro-transferred (Figure 6a and 6b) and electrodeposited (Figure 6c). The electro-transferred lines at 20 and 30 mA·cm<sup>-2</sup> (Figure 6a and 6b, respectively) showing that the lines are well-defined, which line widths of 230-280 µm (the resist-free lines on the tool are between 200 to 240 µm), and have been electro-transferred over the entire area of the A7 substrate with a good uniformity of pattern definition. The electrodeposited lines using the classical methodology (Figure 6c) also showing well-defined lines, which lines width of 205-240 µm (similar to the observed free-resist lines on the tool), along the total area, as could be expected. Therefore, both classical and EnFACE methodologies permits the fabrication of micrometre features with a well-defined shapes. It is important to note the significant improvement of our results at low power and when a non-acidic bath with additives were used to transfer patterns [SS]. However, thickness and roughness analysis were mandatory for a further analysis in order to demonstrate the viability of this methodology, in comparison with classical ones. Thickness of the lines (**Table 3**) were measured over two lines at the same locations where the squares features were electro-transferred (**Figure 7, 5S, 6S, 8S**) showing: (a) reasonable good uniformity definition, as could be seen previously in optical micrographs, and (b) well-defined shapes, especially at the middle of the substrate; providing average thickness of 2.2 µm at 20 mA·cm<sup>-2</sup> (electro-transfer time: 720 s) and 2.0 µm at 30 mA·cm<sup>-2</sup> (electro-transfer time: 480 s), which correspond to electro-transfer efficiencies of 42 % and 39 % and current efficiencies of 60 % and 55 %, respectively. Moreover, the thickness profiles (Figure 7c and **Figure 8S, 9S**) of lines electrodeposited using classical methodology also exhibits good uniformity and very well shape definition, providing an average thickness of 2.8 µm at 20 mA·cm<sup>-2</sup> (electro-transfer time: 400 s), which corresponds to a current efficiency of 87 %. As can be seen the uniformity of the pattern lines using EnFACE methodology is acceptable and comparable with the obtained lines using the classical process as a consequence of the different current density distribution along the entire area. However, the efficiencies showing that this effect was remarkable in EnFACE mode, as a consequence of the current spreading, which affects the real effective area and real effective current density. Therefore, we thought that it could be attributed to the differences in the electrode gap variation along the substrate, as a consequence of the electrodes, which were not perfectly flatten. However, it is important highlight the similar results with both strategies (Figure 7d), which shows that EnFACE technology could be a forthcoming fabrication process.

The average surface roughness amplitude ( $S_a$ ) potted in **Figure 8** and **8S** showed marginally differences in each location (Table 3), which resulting with a reasonable good uniformity in the deposit roughness across the middle lines with EnFACE methodology. As could be expected the average roughness of the electro-transferred at  $30 \text{ mA}\cdot\text{cm}^{-2}$  was slightly rougher than at  $20 \text{ mA}\cdot\text{cm}^{-2}$ . Moreover, it seems that EnFACE methodology permits obtain finer linear patterns at the same current density.

Lastly, **Figure 9** shows optical micrographs of the electrochemical tool after several times that was used as an anode in US conditions. As can be seen at zero uses the electrochemical tool showing the resist and the exposed copper area. After one usage the copper is etched and resist is intact. After five uses copper is etched more and the resist is undercut (black lines). After six and seven uses the resist is delaminating and even more undercut. It is important to see that the electrochemical tool could be used several times. However, up to five times the transfer definition rapidly decay. Lastly, after nine the resist pattern is crazed and delaminating. The main reason for the tool to be unusable is that the resist is delaminating. Figure 9b, 9c show the optical micrographs and profiles of the transferred lines using the electrochemical tool for first and seventh times, respectively. Therefore, it is possible re-use the tool several times, however, up to fifth times the uniformity of the transfer was very poor as a consequence of both ultrasonic power and crazing and delaminating of resist pattern.

Current density / $\text{mA}\cdot\text{cm}^{-2}$	Average deposit thickness / $\mu\text{m}$			Average Roughness ( $S_a$ ) / nm		
	Corners	Middle	All areas	Corners	Middle	All areas
EnFACE methodology						
20	2.1	2.3	2.2	420	214	315
30	1.8	2.3	2.0	521	355	438
Classical methodology						
20	3.2	2.4	2.8	630	249	440

**Table 3:** Thickness, roughness and electro-transfer efficiencies of copper electro-transferred centimetre square features at different locations on an A7 plate substrate using various US powers.

**Figure 6:** Optical micrographs of linear patterns onto A7 plates using US power of  $5 \text{ W} \cdot \text{L}^{-1}$  at (a)  $20 \text{ mA} \cdot \text{cm}^{-2}$  and (b)  $30 \text{ mA} \cdot \text{cm}^{-2}$  by EnFACE methodology and (c)  $20 \text{ mA} \cdot \text{cm}^{-2}$  using classical methodology. Bar scale:  $200 \mu\text{m}$ .

**Figure 7:** 3D thickness profiles of linear electro-transferred patterns at (a)  $20 \text{ mA} \cdot \text{cm}^{-2}$  and (b)  $30 \text{ mA} \cdot \text{cm}^{-2}$  and linear electrodeposited patterns at (c)  $20 \text{ mA} \cdot \text{cm}^{-2}$  under DC conditions at US power of  $5 \text{ W} \cdot \text{L}^{-1}$ . (d) Maximum and average thickness of linear patterns at various locations.

**Figure 8:** 3D Roughness profiles of linear electro-transferred patterns at (a)  $20 \text{ mA} \cdot \text{cm}^{-2}$  and (b)  $30 \text{ mA} \cdot \text{cm}^{-2}$  and linear electrodeposited patterns at (c)  $20 \text{ mA} \cdot \text{cm}^{-2}$  under DC conditions at US power of  $5 \text{ W} \cdot \text{L}^{-1}$ . (d) Average surface roughness amplitude ( $S_a$ ) of linear patterns at various locations.

**Figure 9:** (a) Electrochemical tool at different times used as an anode under US power of  $5 \text{ W} \cdot \text{L}^{-1}$ . Optical micrographs of pattern transfer at various locations at  $20 \text{ mA} \cdot \text{cm}^{-2}$  fabricated by EnFACE methodology using a (b) non-used and (b) seventh times used electrochemical tool.

#### 4. Conclusions

Copper pattern transfer experiments of centimetre square and micrometre lines were performed in 18 L Ultrasonic tank onto large areas (A7 copper plates) using EnFACE technology, which permits testing the scalability viability of EnFACE technology, under DC conditions. Both non-acidic bath (with low content of additives) and low ultrasound power ( $5 \text{ W} \cdot \text{L}^{-1}$ ) were established as a very feasible conditions to electro-transfer various copper patterns, obtaining comparable results with the classical direct electrodeposition using a mask. Electrochemical tool could be used several times as a consequence of both low ultrasound power (at higher power it could be damaged faster) and inhibition of anode passivation due to the chloride. Centimetre square pattern electro-transfer was performed at various ultrasound powers at fixed current density, showing that the better shape definition and electro-transfer efficiencies were attained at  $5 \text{ W} \cdot \text{L}^{-1}$  (average thickness of  $4.4 \mu\text{m}$  and electro-efficiency of 90 %) due to the lower current spreading during the deposition. At 10 and  $30 \text{ W} \cdot \text{L}^{-1}$  average thickness of 3.5 and  $2.6 \mu\text{m}$  and efficiencies of 72 and 54 %, respectively, were achieved. The roughness of the transferred features was 180, 195 and  $130 \text{ nm}$  at 5, 10

and  $30 \text{ W}\cdot\text{L}^{-1}$ , respectively, showing that the main effect was the real current density in each case. Therefore, EnFACE technology permits the scalability of the electro-transfer of centimetre patterns onto large areas.

Linear micrometric pattern electro-transfer were performed at various current densities ( $20$  and  $30 \text{ mA}\cdot\text{cm}^{-2}$ ) and  $5 \text{ W}\cdot\text{L}^{-1}$ , which showing excellent shape definition and acceptable electro-transfer efficiencies ( $42$  and  $39 \%$  at  $20$  and  $30 \text{ mA}\cdot\text{cm}^{-2}$ , respectively). This approach was also compared with the classical electrodeposition process in photolithographed substrates, providing comparable results in terms of shape definition and efficiency ( $59 \%$ ). Roughness analysis show that smoother deposits were obtained at low current density, as expected. Surprisingly, EnFACE patterns exhibited smother surface than the classical ones. Therefore, in this conditions EnFACE technology makes it's a promising microfabrication technology as a consequence of the gain in efficiency by the possibility to re-use the electrochemical tool and competent obtained deposits.

### ***Acknowledgments:***

This work was supported by EU “MESMOPROC” Grant 303550. The Chemical Engineering workshop of CEAM (Newcastle University) is acknowledged for its collaboration. The authors wish to thank the Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB) for allowing us to use their equipment. A.S. would also like to thank the Ministerio de Educación, Cultura y Deporte, for its financial support (FPU grant).

### **References:**

- [1] S. Siau, A. Vervaet, E. Schacht, A. V. Calster, Influence of chemical pretreatment of epoxy polymers on the adhesion strength of electrochemically deposited Cu for use in Electronic Interconnections. J. Electrochem. Soc., 151 (2004) C133-C141.
- [2] Y.-K. Hsu, H.-H. Lin, J.R. Wu, M.-H. Chen, Y.-C. Chen, Y.-G. Lin. Electrochemical growth and characterization of a p-Cu<sub>2</sub>O thin film on n-ZnO nanorods for solar cell application. RSC Adv. 4 (2014) 7655-7659.
- [3] S. Zhong, T. Koch, M. Wang, T. Scherer, S. Walheim, H. Hahn, T. Schimmel. Nanoscale twinned copper nanowire formation by direct electrodeposition, Small 5 (2009) 2265-2270.

- [4] J. Parisi, Y. Liu, L. Su, Y. Lei, In situ synthesis of vertical 3-D copper-core/carbon-sheath nanowalls in microfluidic devices, *RSC Adv.*, 3 (2013) 1388-1396.
- [5] F. Mumm, A. T. J. Van Helvoort, P. Sikorski, Easy route to superhydrophobic copper-based wire-guided droplet microfluidic systems, *ACS Nano*, 3 (2009) 2647-2652.
- [6] M. Hasan, J.F. Rohan, Cu electrodeposition from methanesulfonate electrolytes for ULSI and MEMS applications, *J. Electrochem. Soc.*, 157 (2010) D278-D282.
- [7] M. Cortés, A. Serrà, E. Gómez, E. Vallés, CoPt nanoscale structures with different geometry prepared by electrodeposition for modulation of their magnetic properties, *Electrochim. Acta*, 56 (2011) 8232-8238.
- [8] M. Tian, J. Wang, J. Kurtz, T. E. Mallouk, M. H. Chan, Electrochemical growth of single-crystal metal nanowires via a two-dimensional nucleation and growth mechanism, *Nano Letters* 3 (2003) 919-923.
- [9] A. Serrà, E. Gómez, J. F López-Barbera, J. Nogués, E. Vallés, Green electrochemical template synthesis of CoPt nanoparticles with tunable size, composition, and magnetism from microemulsions using an ionic liquid (bmimPF<sub>6</sub>), *ACS Nano*, 8 (2014) 4630-4639.
- [10] H. Zhou, C. Peng, S. Jiao, W.W. Zeng, J. Chen, Y. Kuang, Electrodeposition of nanoscaled nickel in a reverse microemulsion, *Electrochem. Commun.* 8 (2006) 1142-1146.
- [11] C. Li, T. Sato, Y. Yamauchi, Electrochemical synthesis of one-dimensional mesoporous Pt nanorods using the assembly of surfactant micelles in confined space, *Angew. Chem. Int. Ed.*, 125 (2013) 8208-8211.
- [12] J. B. Nelson, D. T. Schwartz, Electrochemical factors controlling the patterning of metals on SAM-coated substrates, 23 (2007) 9661-9666.
- [13] H.-H. Liu, Y. Liang, H. J. Liu, Regular microarray of Au flower-like structure formed by template-assisted electrodeposition: Influence factors and their electrochemical behavior, *Electrochim. Acta*, 54 (2009) 7514-7518.
- [14] B. Wolfrum, Y. Mourzina, D. Mayer, D. Schwaab, A. Offenhäusser, Fabrication of large-scale patterned gold-nanopillar arrays on a silicon substrate using imprinted porous alumina templates, *Small*, 2 (2006) 1256-1260.
- [15] R. N. P. Colombo, D. F. S. Petri, S. I. Córdoba de Torresi, V. R. Gonçalves, Porous polymeric templates on ITO prepared by breath figure method for gold electrodeposition, *Electrochim. Acta*, 158 (2015) 187-195.

- [16] E. J. Menke, M.A. Thompson, C. Xiang, L.C. Yang, R.M. Penner, Lithographically patterned nanowire electrodeposition, *Nat. Mat.* 5 (2006) 914-919.
- [17] S. Franssila, *Introduction to microfabrication*, 2nd edn. Wiley (2010), West Sussex.
- [18] M. J. Madou, *Fundamentals of microfabrication: the science of miniaturization*, CRC Press (2002), Boca Raton.
- [19] E. W. H: Jager, E. Smela, O. Inganas, Microfabricating conjugated polymer actuators, *Science*, 290 (2000) 1540-1545.
- [20] S. Huang, L. Dai, A. W. H. Mau, Controlled fabrication of large-scale aligned carbon nanofiber/nanotube patterns by photolithography, 14 (2002) 1140-1143.
- [21] A. Shishido, I. B. Divilansky, I. C. Khoo, T. S. Mayer, S. Nishimura, G. L. Egan, T. E. Mallouk, Direct fabrication of two-dimensional titania arrays using interference photolithography, *Appl. Phys. Lett.* 79 (2001) 3332-3338.
- [22] J. Rickerby, J. H. G. Steinke, Current trends in patterning with copper, *Chem. Rev.* 102 (2002) 1525-1550.
- [23] T. Homma, H. Sato, H. Kobayashi, T. Arakawa, H. Kudo, T. Osaka, S. Shoji, Y. Ishisaki, T. Oshima, N. Iyomoto, R. Fujimoto, K. Mitsuda, Sn electrodeposition process for fabricating microabsorber arrays for an X-ray microcalorimeter, *J. Electroanal. Chem*, 559 (2003) 143-148.
- [24] S. Roy, Fabrication of micro- and nano-structured materials using mask-less processes, *J. Phys. D. Applied Physics*, 40 (2007) R413-R426.
- [25] S. Roy, EnFACE: A maskless process for circuit fabrication, *Circuit World*, 35 (2009) 8-11.
- [26] T. Widayatno, S. Roy, Nickel electrodeposition using EnFACE, *J. Appl. Electrochem.* 47 (2014) 807-820.
- [27] Q.-B. Wu, T. A. Green, S. Roy, Electrodeposition of microstructures using a patterned anode, *Electrochem. Commun.* 13 (2011) 1229-1232.
- [28] S. J. Coleman, S. Roy, Electrodeposition of copper patterns using EnFACE technique under ultrasonic agitation, *Chem. Eng. Transactions*, 41 (2014) 37-42.
- [29] S. J. Coleman, S. Roy, Electrodeposition of copper patterns using EnFACE technique under ultrasonic agitation, *J. Appl. Electrochem.* DOI: 10.1007/s10800-015-0823-2.
- [30] T. Kikuchi, T. Uchida, Calorimetric method for measuring high ultrasonic power using water as a heating material, *J. Phys.: Conf. Ser.* 279 (2011) 012012-012017.



- [31] T. Kikuchi, T. Uchida, Ultrasonic power measurement by calorimetric method using water as heating material, IEEE International Ultrasonics Symposium, IUS, 6724830 (2013) 1657-1660.
- [32] Y. Kado, M. Atobe, T. Nonaka, Ultrasonic effects on electroorganic processes. XVIII. A limiting current study on indirect electrooxidation of n-butylamine with a triarylamine redox mediator, Electrochemistry, 68 (2000) 262-266.
- [33] F. Marken, D. L. Goldfarb, R. G. Compton, Sonoelectrochemistry in Highly Resistive Media: Mass Transport Effects, Electroanalysis, 10 (1998) 562-566.
- [34] S. Coleman, S. Roy, Effect of ultrasound on mass transfer during electrodeposition for electrodes separated by a narrow gap, Chem. Eng. Sci., 133 (2014) 35-44.
- [35] J. P. Lorimer, B. Pollet, S. S. Phull, T. J. Mason, D. J. Walton, The effect upon limiting current and potentials of coupling a rotating disc and cylindrical electrode with ultrasound, Electrochim. Acta, 43 (1998) 449-455.
- [36] R. G. Compton, J. C. Eklund, S. D. Page, T. J. Mason, D. J. Walton, Voltammetry in the presence of ultrasound: mass transport effects, J. Appl. Electrochem., 26 (1996) 775-784.