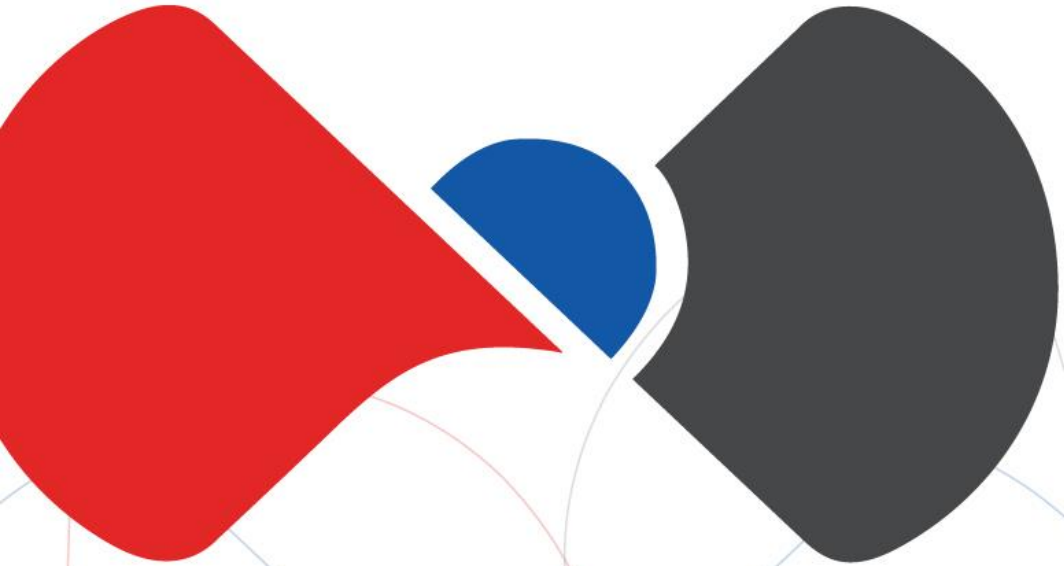
Functional Materials



Optimisation of Process Conditions for the 'Maskless' Electrochemical Patterning of Materials

ICT, Tewkesbury

Andrew J Cobley[1] , Bahaa Abbas[1] , Narinder Bains[1] , Eden Dela Pena[2], Sudipta Roy[2]

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Co-funded by the Eco-innovation Initiative of the European Union

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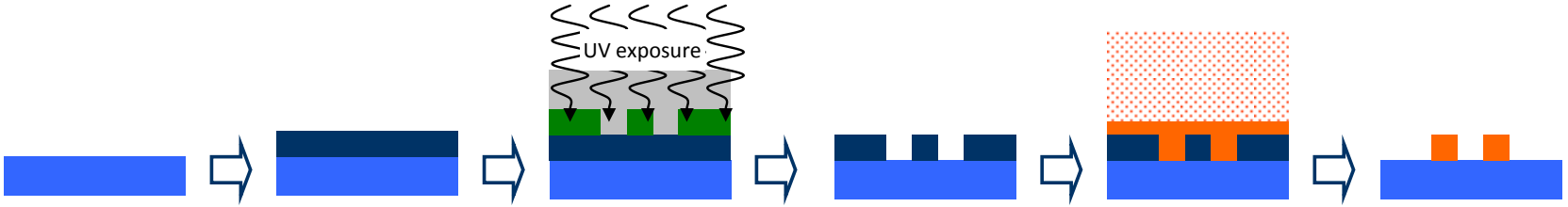
Agenda

- The concept of Electrochemical ‘Maskless’ Patterning –
  - *Initial Laboratory results*
  - *Effect of ultrasound on electrochemical processes*
- The MESMOPROC project
  - *Effect of ultrasound on commercial additives*
  - *Effect of low metal, low acid electrolyte on commercial additives*
- Conclusions

Photolithographic method of patterning metal onto a substrate

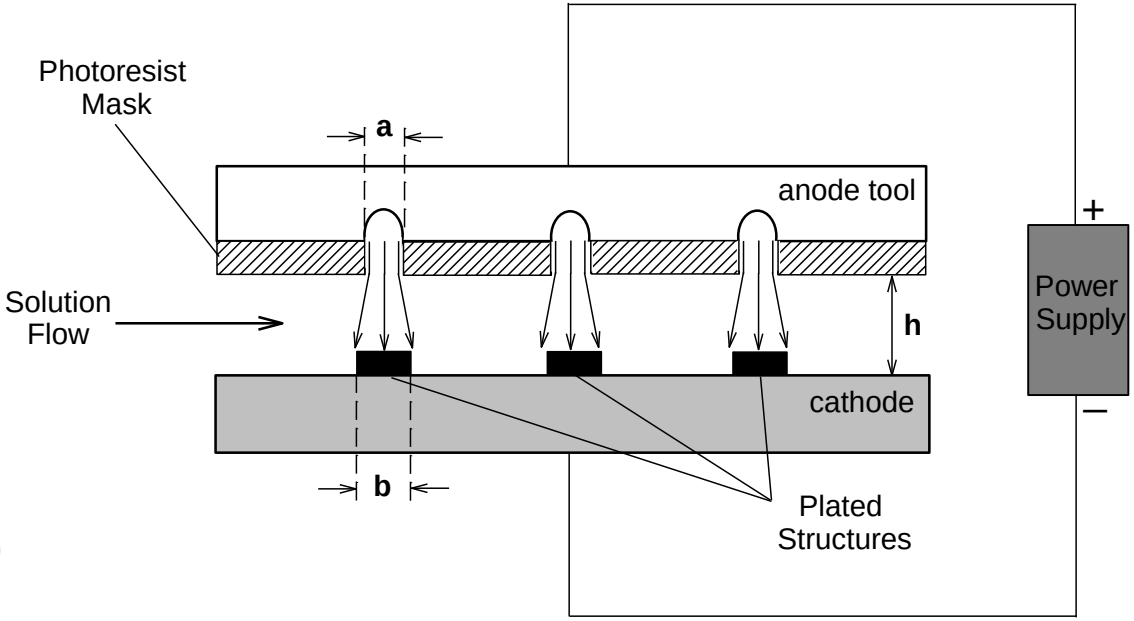


- Long, multiple step process
- Many chemicals required
- Mask cannot be re-used
- Clean room conditions required

Electrochemical Maskless Patterning of Materials

EnFace Technology

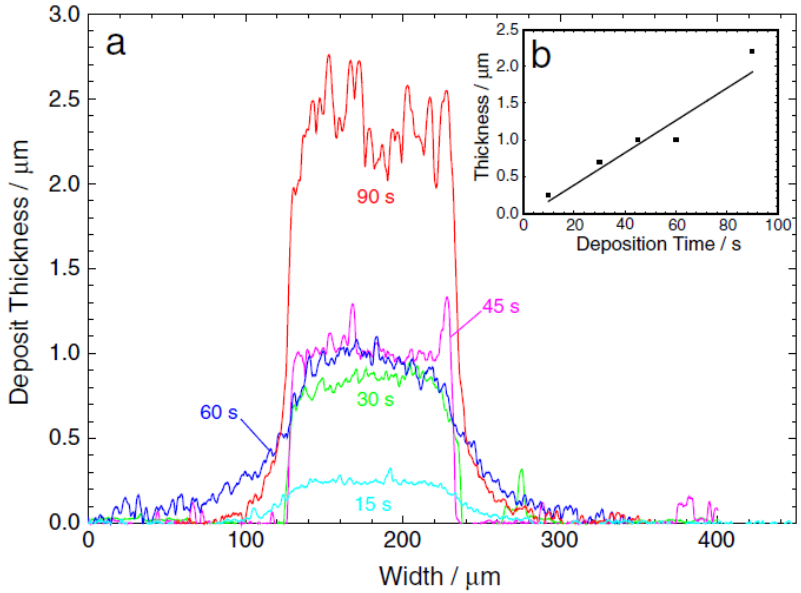
(Electrochemical Patterning by Flow and Chemistry)



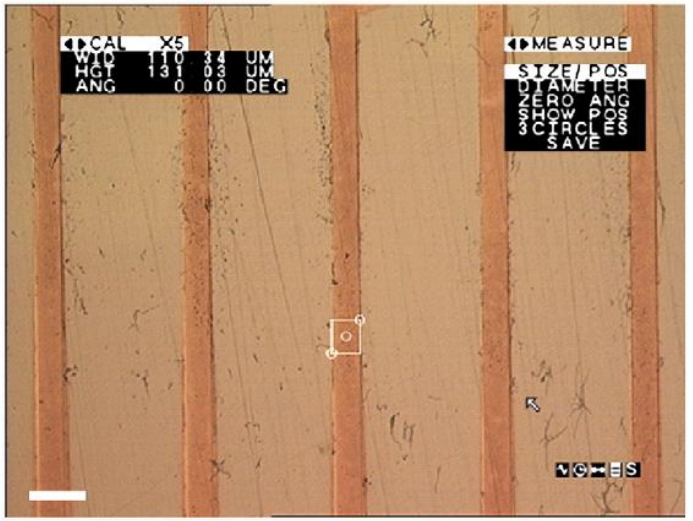
The ‘mask’ is placed on the anode (if plating)
Very small anode to cathode spacing

Electrochemical Maskless Patterning of Materials
Initial Laboratory Studies

In Electrochemical **Plating** experiments it was found that the use of low/no acid electrolyte formulation produced the best image reproduction with very narrow anode-cathode gap



(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.



Images of plated cathodes.
DC plating at 46 mA cm^{-2} for 30 seconds
White scale bar at bottom left corner indicates a width of 200 µm
Electrolyte - 0.1 M $CuSO_4$

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Wu et al, Electrochem. Comm. (2011) 51, 1229-1232 “Electrodeposition of microstructures using a patterned anode”

Conclusions from Initial Laboratory Trials

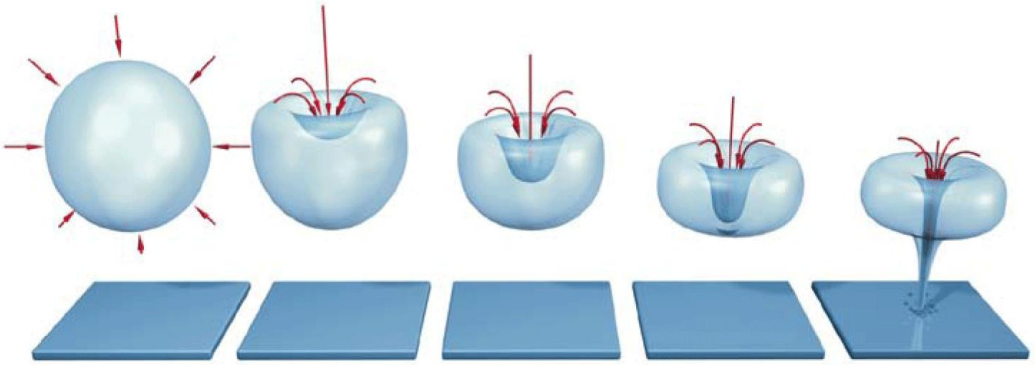
Copper lines patterned on a 2 cm copper disc

- Concept of Electrochemical 'Maskless' selective metallisation of materials proven
- Best reproduction of 'Enface' image occurs using:
  - a narrow anode-cathode spacing
  - a low metal, low acid electrolyte
- Low metal, low acid electrolyte will require good agitation to avoid poor limiting current density and small process window
- High agitation using solution pumping feasible in a beaker but not desirable for first laboratory scale-up

Proposed to introduce low frequency ultrasound to the system to enable high efficiency, focused agitation

Microjetting/Microstreaming

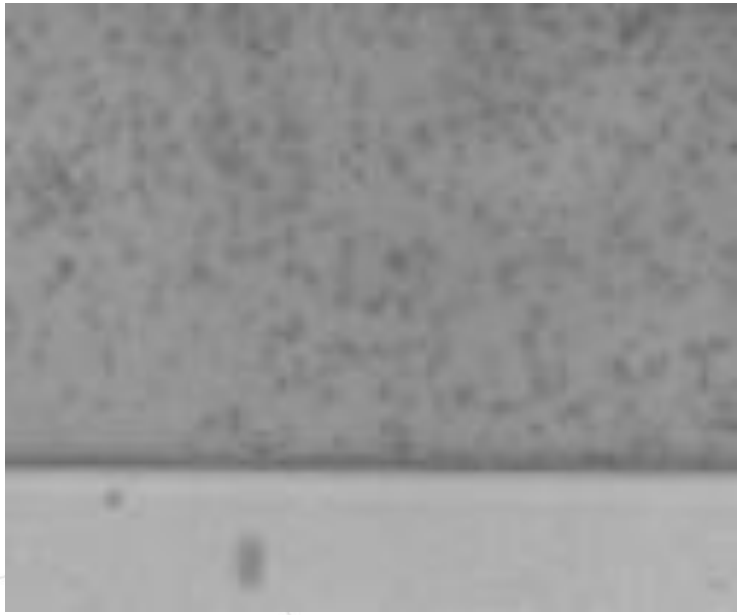
Acoustic Cavitation in a liquid ***NEAR A SURFACE***



ASYMMETRIC COLLAPSE
Inrush of liquid from one side of the collapsing bubble produces powerful jet of liquid targeted at surface

Benefits for Electrochemical Processes

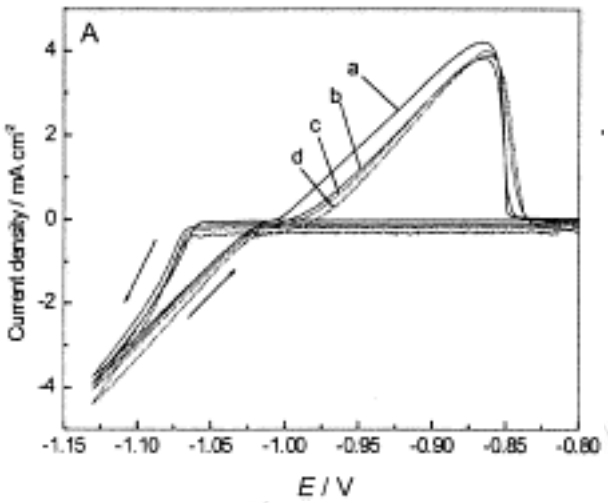
- Thinning of diffusion layer
- Improved mass transport
- Improved solution movement
- Increased limiting current density



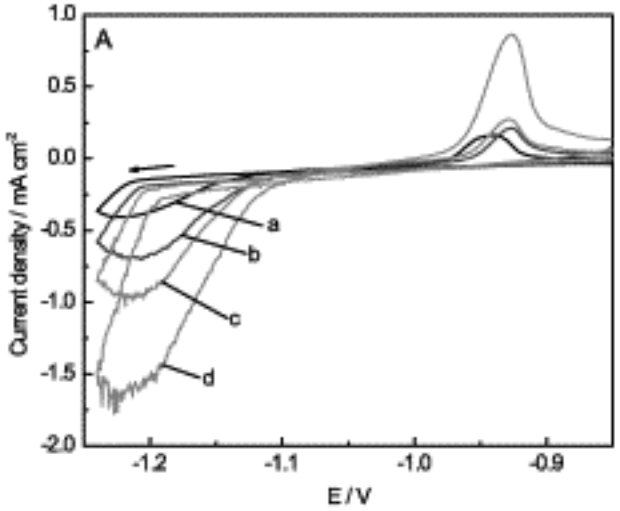
Video courtesy of University of Twente, Netherlands. and Shimadzu Europa GmbH, Duisburg, Germany

Mass Transport

Effect of Ultrasound on CV scan for Zinc deposition
High metal conc.



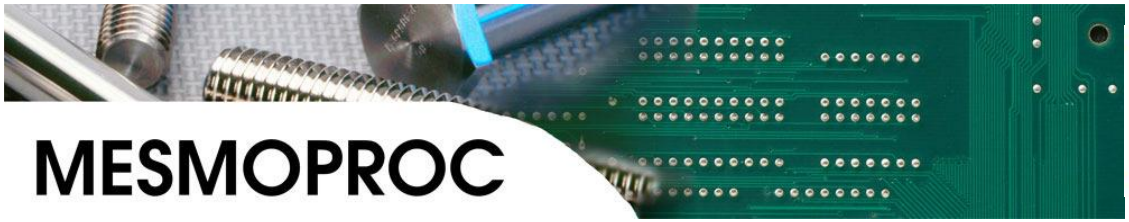
Effect of Ultrasound on CV scan for Zinc deposition
Low metal conc.



(a) silent
(b-d) 20 kHz Ultrasonic Horn with intensities
(b) 37 W cm^2 (c) 78 W cm^2, (d) 238 W cm^2

Data reproduced by kind permission of Elsevier and Prof. Richard Compton, Oxford University
M.E. Hyde, R.G. Compton, Journal of Electroanalytical Chemistry 531 (2002) 19-24

Electrochemical Maskless Patterning of Materials



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The MESMOPROC project aims

•The first application of an innovative new process that combines electrochemical reactor engineering with innovative ultrasound agitation

•To enable selective metallisation of microscale devices, components and printed circuit boards

• Elimination of repetitive conventional photolithography stages

•More details www.mesmoproc.eu

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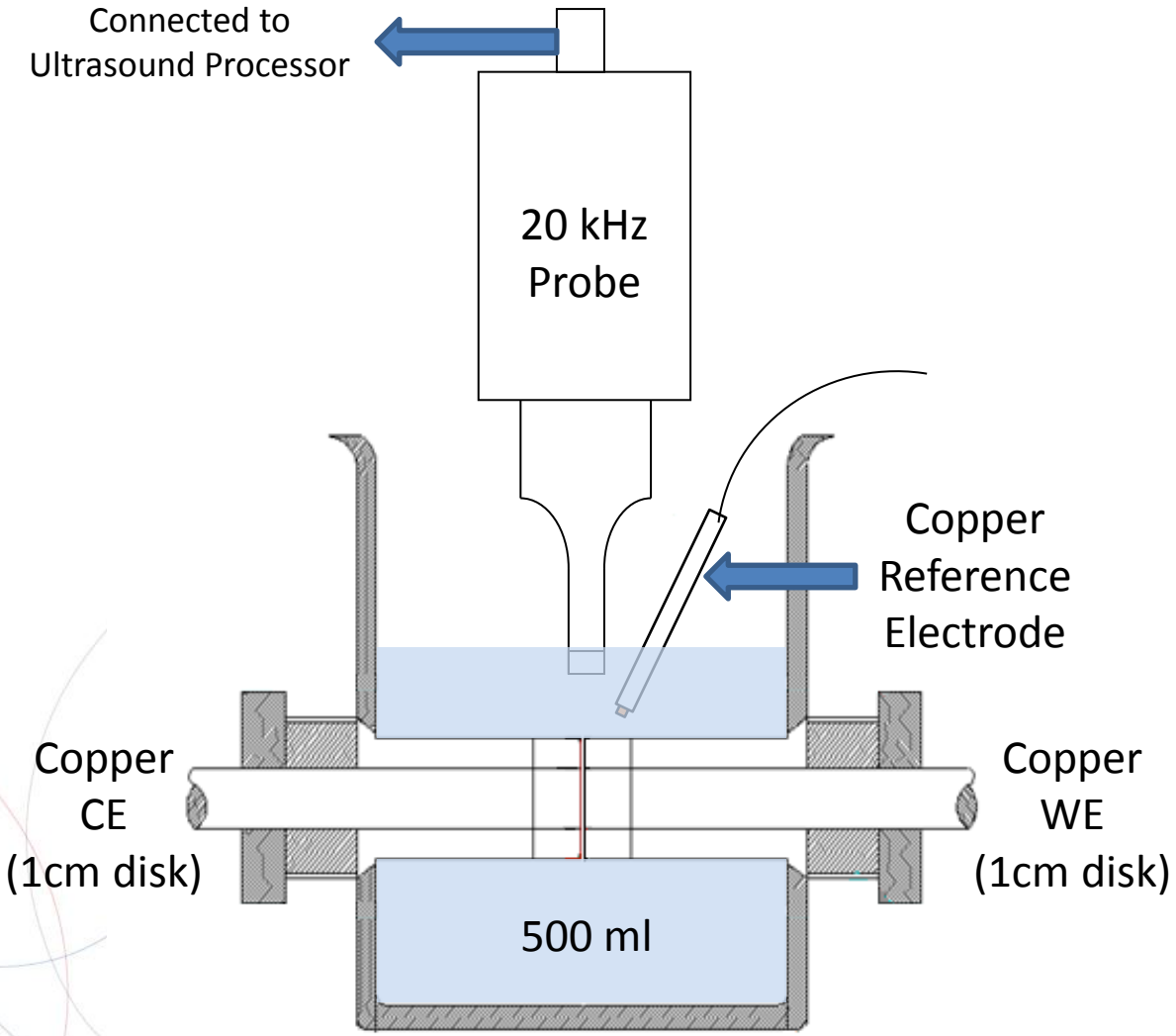
The use of ultrasound to enable focused agitation



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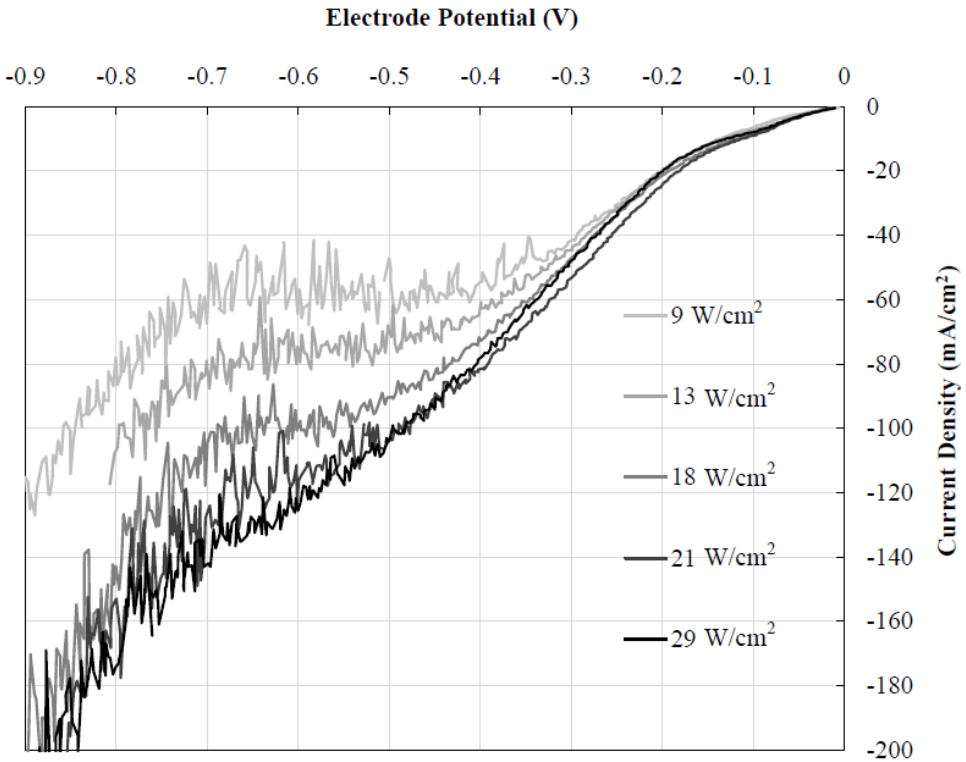
Limiting Current in Lab-scale Reactor



Linear Potential scans with a 0.1 M $CuSO_4$ + 0.1 M H_2SO_4 electrolyte; Scan Rate = 5 mV/s at varying ultrasound intensities (9 - 29 W/cm^2), Electrode gap = 1 cm ; Probe distance = 3 cm.

Limiting current densities at varying probe distances at fixed ultrasonic power of 18 W/cm^2

Probe Distance (cm)	Limiting Current (mA/cm^2)
3	-90
2	-120
1.5	-130

Ultrasound can greatly enhance agitation.
2 pilot scale reactors DBC with integrated ultrasound

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S. Coleman and S. Roy, 2014. Effect of Ultrasound on Mass Transfer during Electrodeposition for Electrodes Separated by a Narrow Gap. Chemical Engineering Science. (under review)

The Effect of Ultrasound on the Additives used in a Commercial Copper Electroplating Electrolyte

Co-funded by the Eco-innovation Initiative of the European Union

The Effect Ultrasound on Acid Copper Electroplating Additives

- MESMOPROC process used ultrasonic agitation
- Desirable that the process can work with standard commercial electroplating solutions
- What would the effect of ultrasound be on a commercial acid copper electroplating additives?
- Study carried out at Coventry University to investigate this question

Copper Gleam Acid Copper Electrolyte

Component	Volume or weight
Deionized water (H_2O)	650 ml/l
Copper Sulfate $CuSO_4$	100g/l
Sulfuric Acid	108 ml/l
Hydrochloric Acid	0.165 ml/l
Copper Gleam HS-200 A	0.3 ml/l
Copper Gleam HS-200 B	10 ml/l

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Experimental Runs

Experiment Number	Ultrasound Frequency (kHz)	Time (minutes)	Power (Watt)	Current Density (A/dm^2)	Current Applied	Electrolysis (Yes or NO)	Copper Anode in solution
1	0 (Silent)	45		NA	NA	No	No
2	20	45	18.81	NA	NA	No	No
3	40	45	19.95	NA	NA	No	No
4	850	45	20.16	NA	NA	No	No
5	0 (Silent)	45		NA	NA	No	Yes
6	20	45	18.81	NA	NA	No	Yes
7	40	45	19.95	NA	NA	No	Yes
8	850	45	20.16	NA	NA	No	Yes
9	0 (Silent)	45		2.5	0.225	Yes	Yes
10	20	45	18.81	2.5	0.225	Yes	Yes
11	40	45	19.95	2.5	0.225	Yes	Yes
12	850	45	20.16	2.5	0.225	Yes	Yes

- Ultrasonic power set to be approximately equivalent at each frequency
- For each set of 4 runs, 1 litre of Copper Gleam was prepared
- For each run 250 ml of electrolyte was used
- Additive consumption measured using a CVS technique

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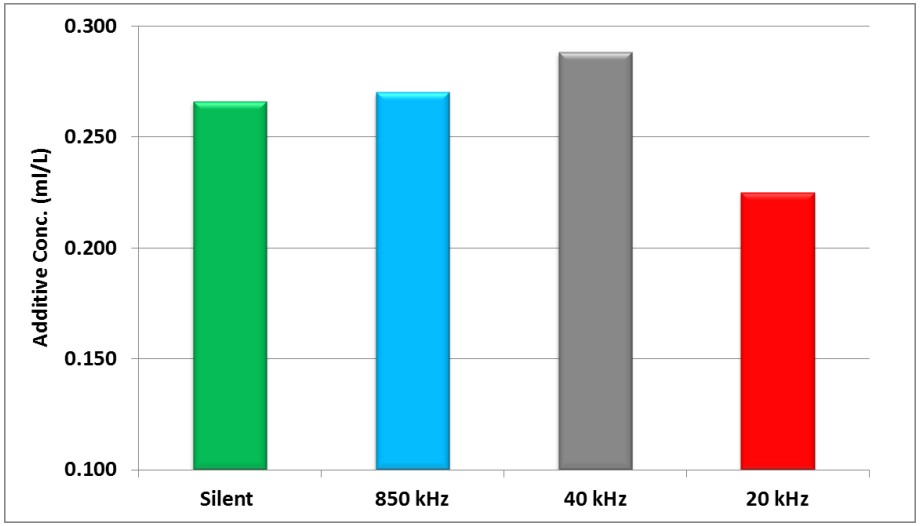
Effect of Ultrasound on Brightener Concentration CVS Analysis

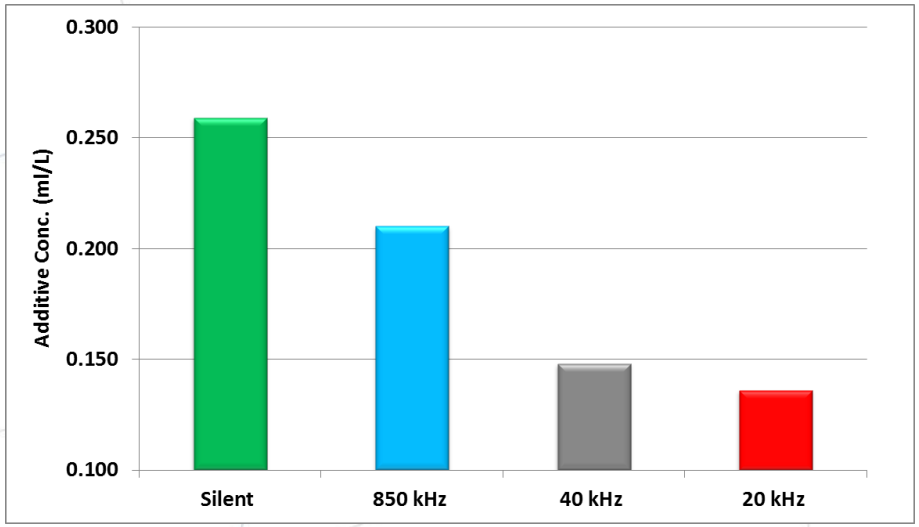
Summary

- Irradiation of the electrolyte with 20 kHz ultrasound can reduce brightener concentration without applied current
- All frequencies of ultrasonic irradiation in conjunction with applied current caused the brightener concentration to be reduced. This was most evident at low frequency (20 and 40 kHz)
- Presence of an anode in solution accelerates brightener reduction particularly in presence of 20 kHz ultrasound

No Electrolysis



With Electrolysis



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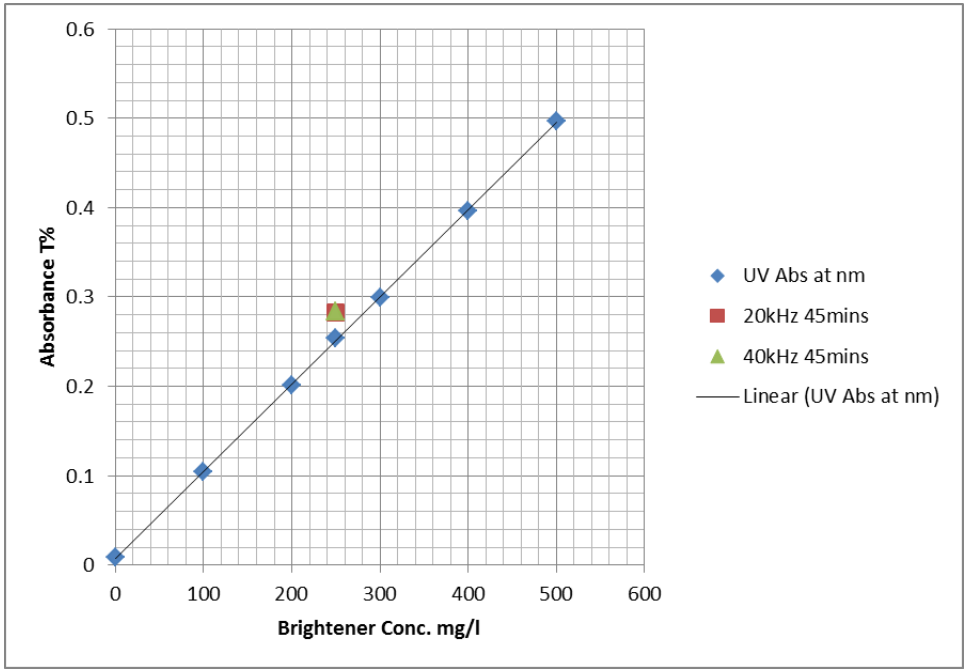
Effect of Ultrasound on Brightener alone
UV-VIS Analysis

Summary

- Irradiation of the 250mg/l brightener alone in DI water treated with 20kHz and 40kHz ultrasound did not reduce brightener concentration



The effect of Low Metal, Low Acid Copper Electrolyte on Commercial Plating bath Additives and Deposit Quality

Effect of Additives on Low Metal, Low acid Electrolyte Deposit Appearance

Normal electrolyte with recommended additive concentrations – bright deposit

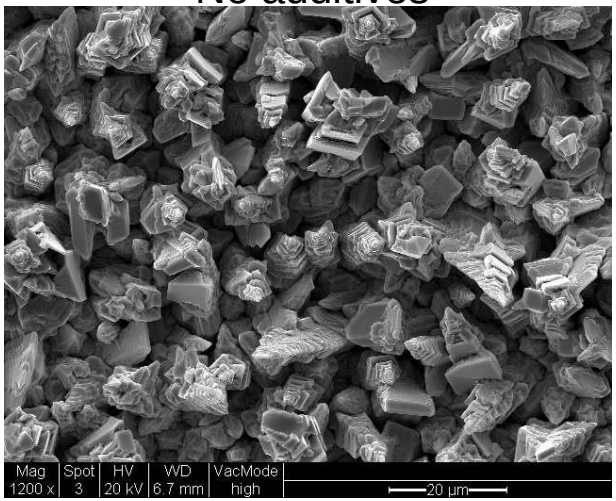
Low acid, low metal electrolyte – no additives, matt deposit

Low acid, low metal electrolyte – increasing additive concentration – deposit becomes fully bright

Effect of Additives on Low Metal, Low acid Electrolyte Grain structure by SEM

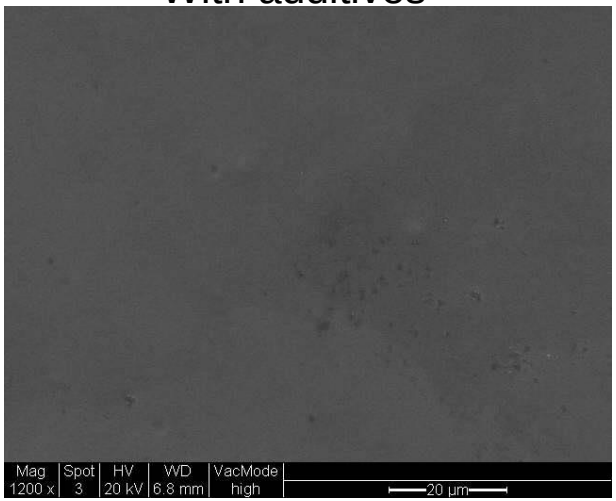
Standard Electrolyte

No additives



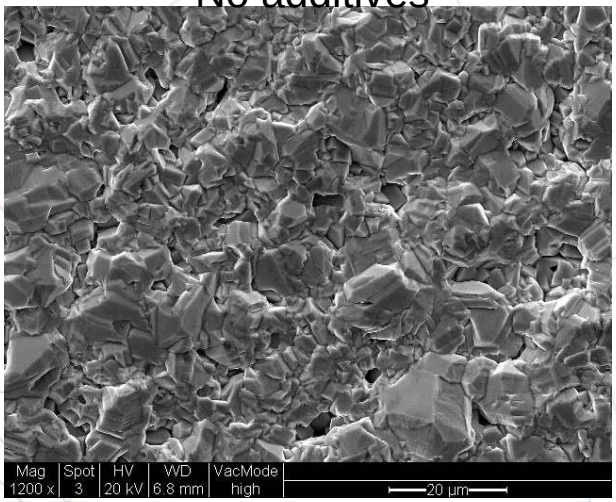
Standard electrolyte

With additives



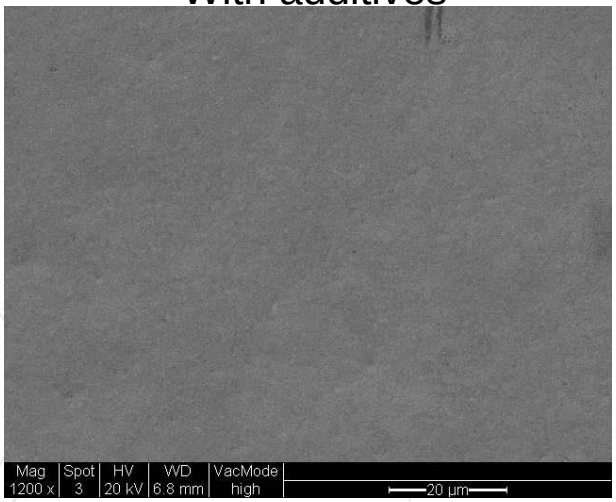
Low metal, Low acid electrolyte

No additives



Low metal, low acid electrolyte

With additives



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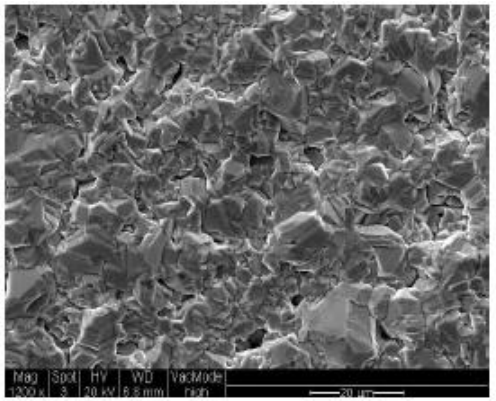
Effect of Additives on Low Metal, Low acid Electrolyte Grain structure by XRD

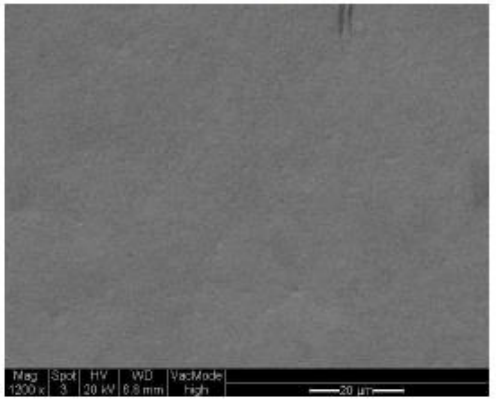
Scherrer's equation and Williamson-Hall technique

Additive concentration	Crystallite size (nm)	Microstrain (%)
0%	1167 ± 129	0.161 ± 0.084
17%	320 ± 55	0.055 ± 0.006
33%	257 ± 90	0.043 ± 0.015
50%	259 ± 72	0.036 ± 0.002
100%	196 ± 12	0.024 ± 0.005
200%	176 ± 3.2	0.021 ± 0.005

As the amount of additive increases, both crystallite size and microstrain decreases



0%



100%

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Effect of Additives on Low Metal Low Acid Electrolyte Summary

- **The use of additives produces a bright, fine grained deposit visually similar to that obtained using a standard electrolyte**
- **Increasing additive concentration reduces grain size**

Overall Conclusions

- **The use of ultrasound in MESMOPROC increases the limiting current density and opens up the process window**
- **Low frequency ultrasound will increase additive consumption**
- **Using a low metal, low acid electrolyte produced good deposit quality with commercial additives**
- **The use of additives in the low metal, low acid electrolyte decreases the grain size**

Scale-Up

An ultrasonic reactor has been designed and built for the MESMOPROC project

Plating trials at:
Pragobord (Czech Republic) – PCB manufacturer

Protection des Metaux (France) – high tech electroplating company

Ultrasonic tank (left) connected to ultrasonic generators with control panel (right)

Training session on pilot plant at PROMET with plating technicians and Production Manager, by Jacques Halut

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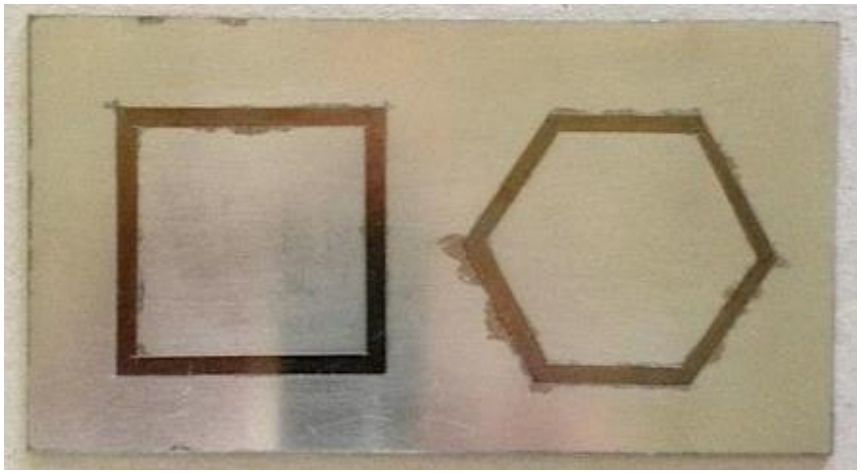
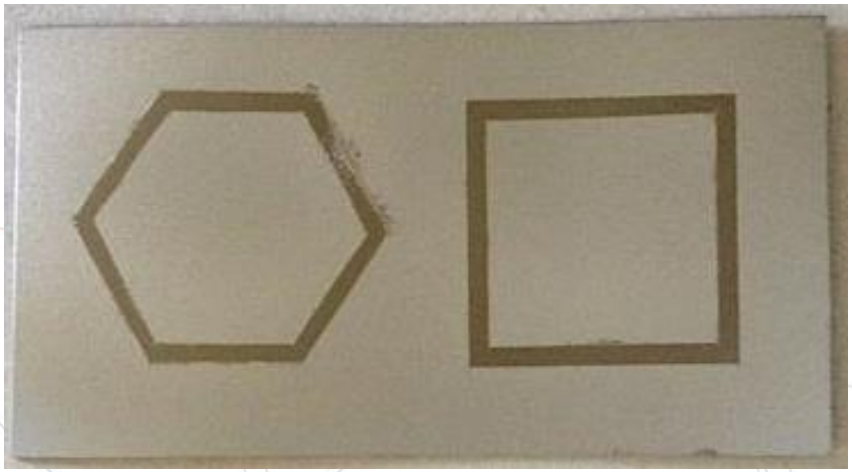
Initial PROMET trials

Image Transfer of Square and Hexagonal shapes to produce electronic grids



- Plated in Nickel Sulphamate solution
- Plating thickness 20 µm
- Some over-plating at cathode



- Increased ultrasonic power
- Much improved image transfer

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Functional Materials

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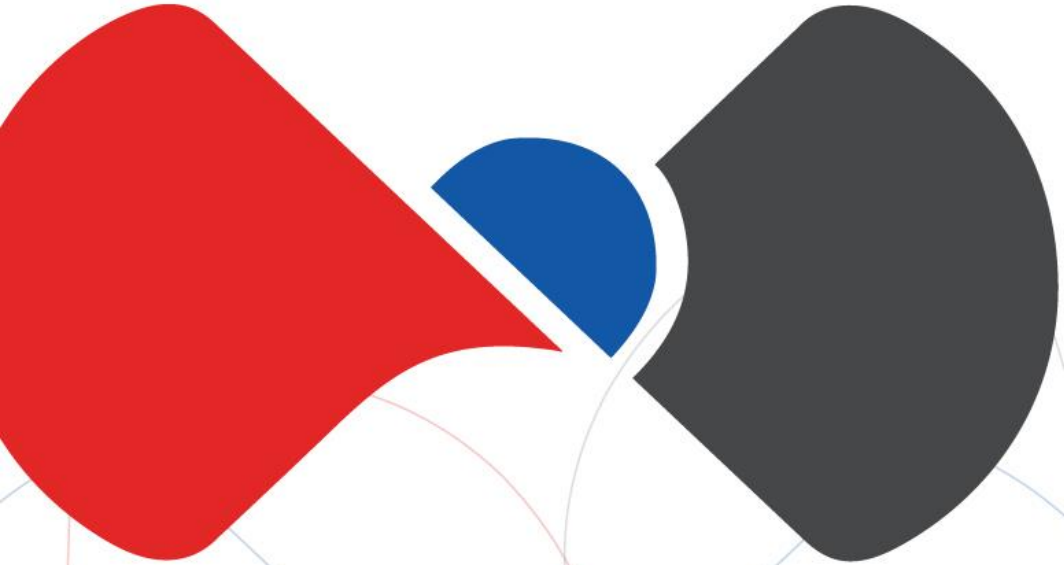

Thank you

Any Questions ?

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Source: The Times and The Sunday Times Good University Guide 2014/2015