1 **Effect of Additive Concentration during Copper Deposition using EnFACE Electrolyte**

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10 **Abstract**

11 Copper deposition from solutions using high concentration of acid, metal ions and
12 polyethylene glycol (PEG), and bis-(3-sulfopropyl) disulfide (SPS) and chloride ions (Cl^-) is
13 well known. A recent maskless micropatterning technology, which has the potential to
14 replace traditional photolithographic process, called EnFACE, proposed using an acid-free,
15 low metal ion solution which is in direct contrast to those used in standard plating
16 technology. In this work copper has been deposited using standard electroplating solutions
17 and those used in the EnFACE process. In the standard electrolyte 0.63 M $CuSO_4$ and 2.04 M
18 H_2SO_4 has been used, along with Gleam additives supplied by Dow Chemicals. For the Enface
19 electrolyte, copper deposition has been carried out using without any acid, and with
20 different concentrations of additives between 17% - 200% of those recommended by
21 suppliers. 25 um of metal has been plated on stainless steel coupons as suggested by and
22 ASTM, peeled off and subjected to ductility and resistance measurements. Scanning
23 electron microscopy and electron back scatter diffraction has been carried out to determine
24 the deposit morphology. It was found that copper deposits obtained from acid-free
25 solutions containing low concentration of metal ion and additives produced copper deposits
26 had properties which are comparable to those obtained from standard electrolytes. The
27 optimum additive concentration for the EnFACE electrolyte was 50% of the recommended
28 value.

Keywords: EnFACE process, copper film, additives, electrodeposition, electroplating.

1.0 Introduction

Copper is the standard metal used in wiring printed circuit boards [1] and interconnects in electronic devices [2]. The standard manufacturing process for both these technologies uses electrodeposition. It is well established that the electrodeposition processes employ electrolyte chemistry of high metal and acid concentrations and employ additives, which impart desirable properties to the plated copper [3]. Numerous studies geared on understanding the role of additives in electroplating have concluded that these chemicals are essential to obtaining metal deposits of high quality [4-9].

Recently a new mask-less process, called EnFACE, has been proposed to deposit microscale copper features [10]. As opposed to the standard electrolytes used for PCB and electronic manufacturing, EnFACE proposed a solution using 0.1 M $CuSO_4$ and no acid [10-15]. Since most of the current literature is has been focused on in understanding the role of additives in the established processes [16-19], the effect on this new chemistry on deposited copper is still unknown. In addition, it is unclear how much additive is required to change deposit properties and what effect they would have on the deposit.

This work examines the effect of additives on deposit properties when copper is deposited from EnFACE electrolyte and when additives are added to the bath. The additives used were Gleam A and B (Dow Chemical) which are used in printed circuit board manufacturing. The EnFACE electrolyte consisted of a 0.1 M $CuSO_4$ solution without addition of acid. Additive levels of 17%, 33%, 50%, 100% and 200% of that recommended by the supplier were added to the solution. In addition, a solution of 0.63 M $CuSO_4$ with 2.04 M H_2SO_4 with additives as per supplier recommendations was also used in plating experiments.

Copper films of 25 um have been plated on polished steel coupons tests in a beaker without agitation. Deposits were plated from different electrolytes and subjected to ductility and resistivity tests. Deposit morphology was examined by scanning electron microscopy and electron back scatter diffraction. Yield strength and sheet resistance were measured to compare deposit properties against those recommended by Institute of

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58 Interconnecting and Packaging Electronic Circuits. Deposit properties are interpreted in
59 terms of additive concentration in the bath. The effectiveness of using low concentrations of
60 metal ions and additives on the influence deposit properties has been assessed.

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62 **2.0 Experimental**

63 **2.1 Apparatus**

64 Electrodeposition experiments were carried out using a traditional two-electrode
65 plating set-up. The working electrode was a dog-bone shaped stainless steel coupon with an
66 area of 31.92 cm^2. The counter electrode was a copper rod with an exposed area of 58.1
67 cm^2. Plating was done in a 2-litre cell using the appropriate plating solution, and the current
68 source was a Thurlby Thundar PL-310 power unit.

69

70 Morphological analysis (SEM and EBSD) was done using the JEOL JSM-5300LV.
71 Resistivity of the plated films were measured using the Signatone Pro4 (four point probe)
72 system in the Electronics and Electrical Engineering department Newcastle University UK.
73 Mechanical properties were characterized using a Tinius Olsen H50KS with Horizon software
74 for data recording. All tensile tests followed the ASTM E-345 [20], a standard for
75 determining tensile properties of metallic films. Morphological and mechanical
76 characterization were conducted in the Advanced Chemical and Materials Analysis (ACMA)
77 laboratory, Newcastle University.

78

79 **2.2 Chemicals and Electrolytes**

80

81 Steel coupons (308 stainless) were manufactured to the specifications of IPC-TM-650
82 (IPC-TM stands for The Institute for Interconnecting and Packaging Electronic Circuits
83 Testing Methods) standard. Technical grade $CuSO_4$ and H_2SO_4 (Sigma-Aldrich) were used to
84 prepare the plating electrolyte. The additives used were commercially available Copper
85 Gleam series (Rohm Haas). Copper Gleam HS – 200 A served as the accelerator (SPS), while
86 Copper Gleam B was the inhibitor (PEG). The Cl^- ions were sourced from concentrated HCl
87 (37%, Sigma Aldrich). Chemicals for pre-treatment of the coupons include concentrated

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HNO_3 and ethanol (Sigma Aldrich). The PRP200 photoresist (Electrolube) was used to insulate the backside of the coupons. Table 1 lists the composition of the different plating baths used for copper deposition.

2.3 Procedure

Prior to actual plating, the stainless steel coupons were cleaned with concentrated HNO_3, and then rinsed with water for 1 minute. The coupons were mechanically polished using silicon carbide sheets, starting at grit #220 and progressing to grit #4000. One side of the coupon was coated with the photoresist, and left to dry. The exposed side of the coupon was swabbed with ethanol for 30 seconds and again allowed to dry.

Electrodeposition was carried out in direct current (DC) mode. The counter and working electrode was set-up in the plating cell containing different electrolytes. Table 2 shows the plating parameters used for the different experiments. These parameters were derived from polarization experiments that yielded limiting current regarding each bath type. Since the deposits become rougher as they approach the limiting current [21], the current was set at a fraction of this value to ensure that dendritic copper was not plated. The total plating time was calculated to obtain a copper film with thickness of 25 um.

After the allotted deposition time was reached, the coupons were removed from the solution and washed with deionized water for 1 minute. The surface was dried using a lint free cloth and left to dry in air. The plated copper films were then carefully peeled off from the stainless steel substrate, and were prepared for subsequent characterization. Each experiment was repeated three times to check for reproducibility.

For SEM and EBSD analysis, a 2x2 cm^2 area was cut out from the central portion of the copper coupon. For mechanical and resistivity testing, the whole coupon was used. Necessary care was taken to prevent damage on the coupons, particularly during handling and specimen mounting in the UTM that would compromise the quality of results of the mechanical tests. The values reported in this manuscript are the average of measurements from three different films.

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3.0 Results and Discussion

3.1 Morphology and Grain Size Measurements

Figure 1 shows the SEM images (planar view) of the products of the EnFACE bath with different additive concentration and the standard bath. It can be observed that as the amount of additive increased, the surface roughness of the deposit from the EnFACE bath noticeably decreased. In fact, the product of the bath with 100% and 200% additive concentrations appeared the smoothest and most compact among the lot. On the other hand, in terms of appearance, the deposit from the standard copper bath is similar to that of the E-33 and E-50 EnFACE bath, which showed that even at low concentrations the influence of additives is substantial.

The observed reduction in surface roughness may indicate the occurrence of a fine-grained structure in the deposit. However, attempts to quantify the grain size of the copper films proved difficult since the grain structures were not easily discernible, even when viewed at high magnifications. Therefore, it became necessary to use another imaging technique that allowed accurate visualization of grain morphology. Electron back-scatter diffraction (EBSD) was chosen because the technique allows grain size and grain orientation analysis without the need to alter the surface condition of the metal.

Figure 2 shows the corresponding EBSD maps for the products of the EnFACE bath with different levels of additive concentration, and of the standard copper bath. The EBSD images revealed the grain structure, which were predominantly equiaxed for the electrolyte without additives, and becomes smaller as additive concentration is increased. The EBSD data allowed measurement of the grain size of deposits.

The rightmost column in Table 2 gives a summary of the calculated grain size of deposits measured using the EBSD image analyzing software TANGO (HKL Technology A/S, 2001). The grain structure map produced in EBSD was processed by performing noise reduction and wild spikes extrapolation. The band contrast was adjusted to clearly see the grains. The grain size parameter used is the major and minor axis of the fitted ellipse and the software automatically measures the grain size based on the delineation of all of the grain boundaries.

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Similar to the conclusions made from SEM analysis, the EBSD results indicated that additives created a finer grain structure in the deposit, and that the decrease in grain size was proportional to the concentration of additives used. The appearance of small grains inside the larger ones was further analyzed, and these small grains were identified as sub-grains brought about by recrystallization. Dynamic recrystallization or self-annealing is a recognized phenomenon that exclusively occurs in copper plated from additive-containing electrolytes [22].

The SEM and EBSD results validate the grain-refining action of additives on the copper deposits. While numerous studies have reported similar observations in conventional copper baths [23, 24, 25], these observations may be the first report on the effect of additives used for super-filling on the products of the EnFACE bath. It is also observed that the grain refining effect of additives on the EnFACE bath is more pronounced than in the standard bath. This was seen with the finer grain size obtained in the EnFACE copper compared to the standard copper at the same additive concentration.

Grain refinement is one of the most important morphological and structural effects of additives [24]. It is known that additives affect the mechanisms of nucleation and growth during plating [26]. For example, brighteners enhance nucleation rates, while leveling agents inhibit dendritic growth. Both these actions can contribute to creating the fine-grained structure seen in the deposits. The effect could even be synergistic when different types of additives are present in the electrolyte. Since, grain refinement would affect the mechanical and electrical properties, these properties were measured and are reported below.

3.2 Mechanical and Resistance Measurements

Figure 3 shows the resistivity measurements for different additive concentration using EnFACE electrolyte. Clearly, the progressive addition of additives created a more resistive copper deposit. Furthermore, the resistivity of some of the EnFACE copper is similar in value to copper deposited from a standard electrolyte; i.e., the resistivity is 2.27 μohm-cm when copper is plated from a standard bath, and 2.30 and 2.31 μohm-cm when deposited from E-33 and E-50, respectively.

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176 The increase in the resistivity of the copper film is explained by the significant
177 reduction of grain size brought about by additive use. Morphological analysis presented
178 earlier has already confirmed a change in grain size. Grain boundaries, together with other
179 defects, act as electron scattering centers and reduce the effective displacement of the free
180 electrons during electronic conduction [27]. Thus, the increase in grain boundary area
181 during grain refinement caused the increase resistivity of the deposited film.

182 Figure 4 shows the plot of mechanical properties; namely, 0.2% offset yield strength
183 (YS), ultimate tensile strength (UTS), and the ductility of the electrodeposited copper films,
184 as a function of additive concentration. The results reveal the strong effect of additive
185 concentration on mechanical properties. Both YS and TS increased while ductility decreased
186 with increasing additive concentrations. The percent increase in YS and TS, and the %
187 decrease in ductility are almost similar; a ~40% change in value from the lowest to the
188 highest additive concentration.

189 Table 3 summarises the mechanical properties of copper plated from a standard
190 bath. The Institute for Interconnecting and Packaging Electronic Circuits advises that copper
191 for interconnects to have a minimum tensile strength of 207 MPa and ductility of 3% [28].
192 Using these values, it can be seen that plated films from EnFACE electrolytes are closer to
193 the specification of the Institution than those obtained from the standard electrolyte. It is
194 envisaged that by optimising bath and plating conditions, the specifications for
195 interconnections and packaging can be achieved.

196 The observed trends in the plated copper are consistent with the well-known
197 mechanical behavior of metals. Typically, an increase in the metal's strength will be
198 accompanied by a loss in ductility. The results also indicate a clear improvement in the
199 mechanical strength of the plated copper when additives are used with the bath. To explain
200 how additive concentration affects mechanical properties, one needs to consider the plated
201 metal's inherent microstructural features. Important microstructural features include
202 dislocation, grain boundaries and voids [25].

203 It is reasonable to assume that the observed grain size refinement directly caused
204 the changes in the metal's yield strength and ductility; a statement consistent with
205 published work [29, 30, 31]. Classical theories on slip and plastic yielding explain how grain

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206 boundaries can serve as dislocation barriers, thereby lowering dislocation mobility and
207 preventing easy plastic deformation to occur. Consequently, such an action increases YS and
208 lowers ductility. Tensile strength, on the other hand, is strongly affected by the amount of
209 voids, and an inverse relation exists between the two.

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211 **3.3 Optimum Additive Concentration**

212 By inspecting the properties of the copper plated from EnFACE electrolytes
213 containing different concentration of additives, it was found that at an additive
214 concentration of 50%, the plated copper has properties close to the specifications stated by
215 IPC. Though the properties of the E-50 electrolyte is slightly different from the values
216 specified, they are closer than those obtained from a standard electrolyte. It can be
217 envisaged that further improvements in deposit properties could be obtained by optimising
218 plating conditions.

219 Notably, the EnFACE electrolyte has a low metal ion concentration, which can limit
220 plating rates (c.f. Table 2). In fact, the plating rate of the standard electrolyte is nearly four
221 times higher than the best EnFACE electrolyte (E-50). This means that the rate of plating
222 needs to be increased by improving agitation. In many industries, such as circuit board
223 manufacturing, plating rates of 1.5-2.0 ASD (15 - 20 mA/cm^2) are advised. Since all of the
224 EnFACE electrolytes exceed this plating rate, it should not affect plating rates in an industrial
225 environment. On the other hand, by operating baths which have low metal and additive
226 concentration, savings and sustainability can be achieved.

227

228 **4.0 Conclusions**

229 Copper was successfully plated from the additive containing EnFACE bath, and its
230 properties were characterized and compared to that achieved using a standard electrolyte.
231 Stainless steel coupons were plated with 25 um copper films using electrolytes of different
232 additive concentrations. Additives caused the refinement of the grain structure of deposits,
233 and the decrease in grain size was proportional to the concentration of additive used. This
234 grain refinement consequently increased resistivity, yield and tensile strength, and reduced

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235 the ductility of plated copper. The EnFACE bath required a lower amount of additive to
236 obtain a product that has comparable properties to that obtained from a standard
237 electrolyte. The optimum additive concentration appears to be about 50% lower than the
238 industry recommended dosage.

239

240 **Acknowledgement**

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244 their affiliation to Strathclyde University.

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304 **Figure Captions**

305 Figure 1: SEM images of copper deposits from EnFACE bath with different additive
306 concentration: a) E-17 with 17% additive concentration, b) E-33 with 33% additive
307 concentration, c) E-50 with 50% additive concentration, d) E-100 with 100% additive
308 concentration and e) E-200 with 200% additive concentration, and f) S - standard bath.
309 These percentages are relative to the industry recommended additive concentration of 10
310 ml/L Copper Gleam B, 0.5 ml/L Copper Gleam A, and 70 ppm Cl^-.

311

312 Figure 2: EBSD images of copper deposits from EnFACE bath with different additive
313 concentration: a) E-17 with 17% additive concentration, b) E-33 with 33% additive
314 concentration, c) E-50 with 50% additive concentration, d) E-100 with 100% additive
315 concentration and e) E-200 with 200% additive concentration, and f) S - standard bath.
316 These percentages are relative to the industry recommended additive concentration of 10
317 ml/L Copper Gleam B, 0.5 ml/L Copper Gleam A, and 70 ppm Cl^-. The calibration bar is for 2
318 um length. The different colors in the EBSD map represent different crystals planes as
319 described by the g) inverse pole legend.

320

321 Figure 3: Resistivity measurements of electrodeposited copper films using EnFACE
322 electrolyte with varying additive concentrations.

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324 Figure 4: The a) yield strength, b) tensile strength and ductility of plated copper films using
325 EnFACE electrolyte with varying additive concentrations.

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335 **Table 1: Bath composition and nomenclature.**

Designation	Setting description	Cu_2SO_4 M	H_2SO_4 M	Gleam B ml/L	Gleam A ml/L	HCl ppm
S	Standard bath	0.63	2.04	10	0.5	70
S-0	Standard bath without additives	0.63	2.04	X	X	X
E-0	EnFACE bath without additives	0.1	X	X	X	X
E-17	17% of the recommended additive concentration	0.1	X	1.7	0.08	12
E-33	33% of the recommended additive concentration	0.1	X	3.3	0.17	23
E-50	50% of the recommended additive concentration	0.1	X	5.0	0.25	35
E-100	Recommended additive concentration	0.1	X	10.0	0.50	70
E-200	High concentration (double of the recommended additive)	0.1	X	20.0	1.0	140

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337 "S" stands for "standard" electrolytes based on supplier recommendation and "E" stands for
338 "Enface" baths. The number following the "S" and "E" stand for the percent of additive
339 concentration added to the electrolyte

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342 **Table 2: Plating parameters**

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Electrolyte	Plating current mA (40% from I_{LIM})	Plating time minutes	Grain size From EBSD (nm)
S	245	146	431
S-0	255	152	11524
E-0	68	615	9016
E-17	68	623	758
E-33	63	623	523
E-50	58	669	466
E-100	54	705	407
E-200	53	708	400

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358 **Table 3: Mechanical properties of copper plated from S, S-0 and E-50 bath.**

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Bath	$YS_{0.2\%}$, MPa	TS, MPa	Ductility, %
S	219	256	1.69
S-0	136	145	2.77
E-50	170	213	2.17

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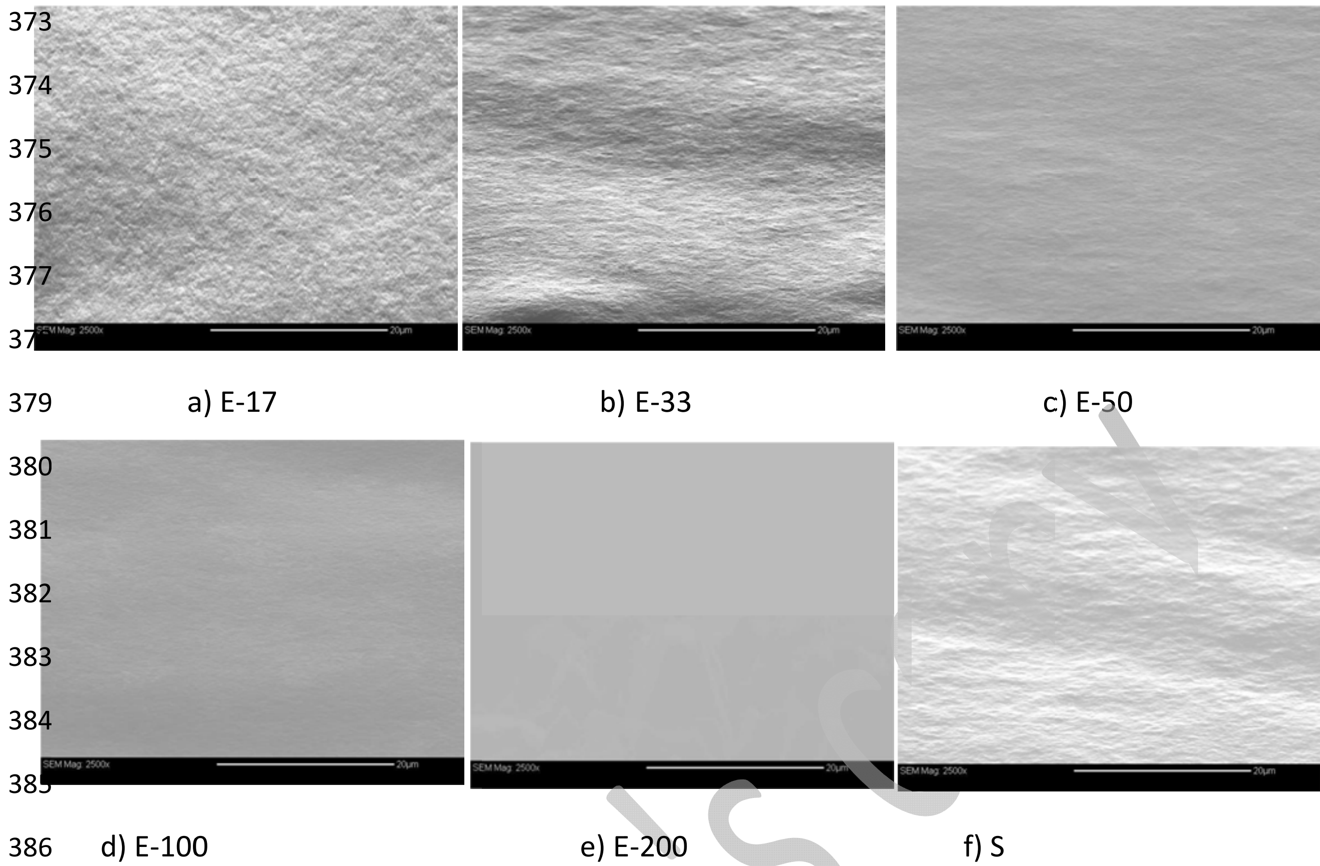
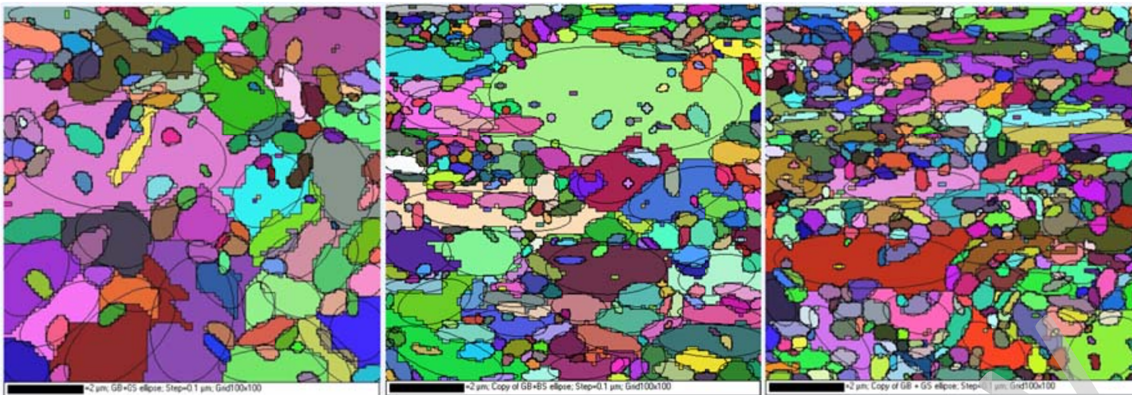
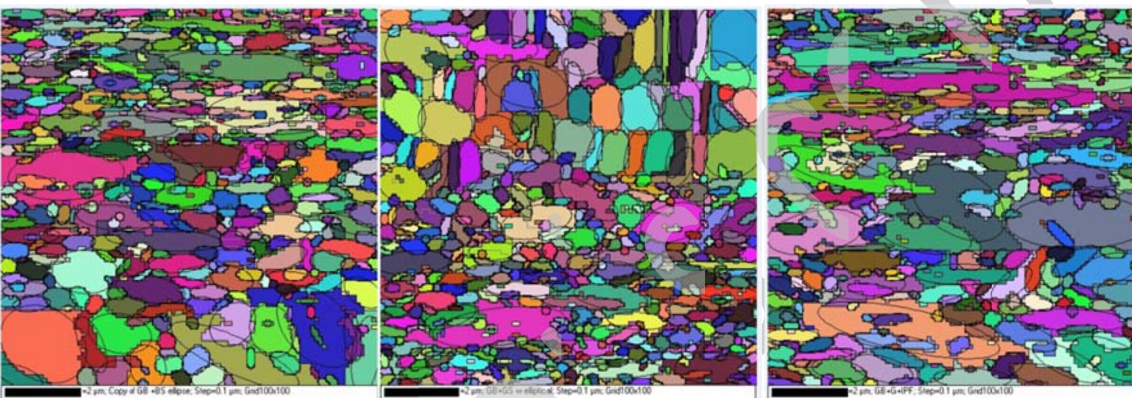


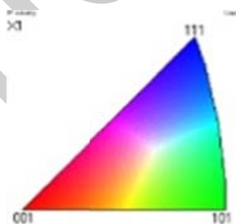
Figure 1: SEM images of copper deposits from EnFACE bath with different additive concentration: a) E-17 with 17% additive concentration, b) E-33 with 33% additive concentration, c) E-50 with 50% additive concentration, d) E-100 with 100% additive concentration and e) E-200 with 200% additive concentration, and f) S - standard bath. These percentages are relative to the industry recommended additive concentration of 10 ml/L Copper Gleam B, 0.5 ml/L Copper Gleam A, and 70 ppm Cl^-.



a) E-17 b) E-33 c) E-50



d) E-100 e) E-200 f) S



g) Inverse pole legend

Figure 2: EBSD images of copper deposits from EnFACE bath with different additive concentration: a) E-17 with 17% additive concentration, b) E-33 with 33% additive concentration, c) E-50 with 50% additive concentration, d) E-100 with 100% additive concentration and e) E-200 with 200% additive concentration, and f) S - standard bath. These percentages are relative to the industry recommended additive concentration of 10 ml/L Copper Gleam B, 0.5 ml/L Copper Gleam A, and 70 ppm Cl^-. The calibration bar represents a length of 2 um. The different colors in the EBSD map represent different crystals planes as described by the g) inverse pole legend.

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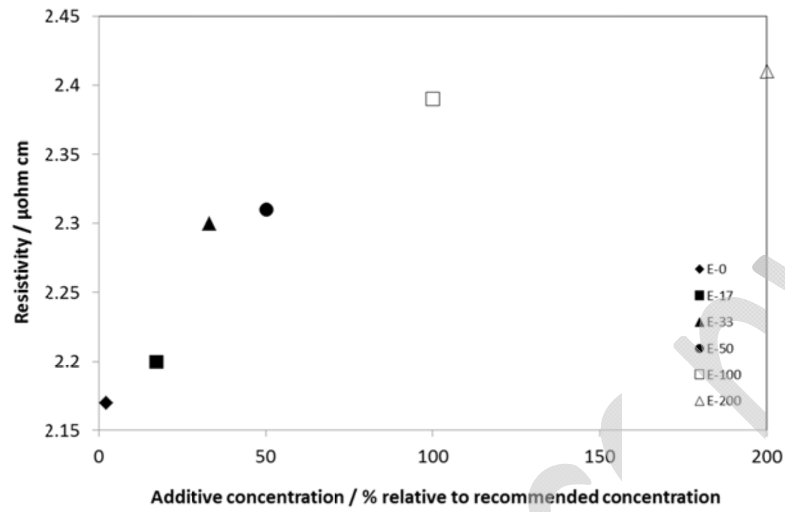

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437 **Figure 3: Resistivity measurements of electrodeposited copper films using EnFACE**
438 **electrolyte with varying additive concentrations.**

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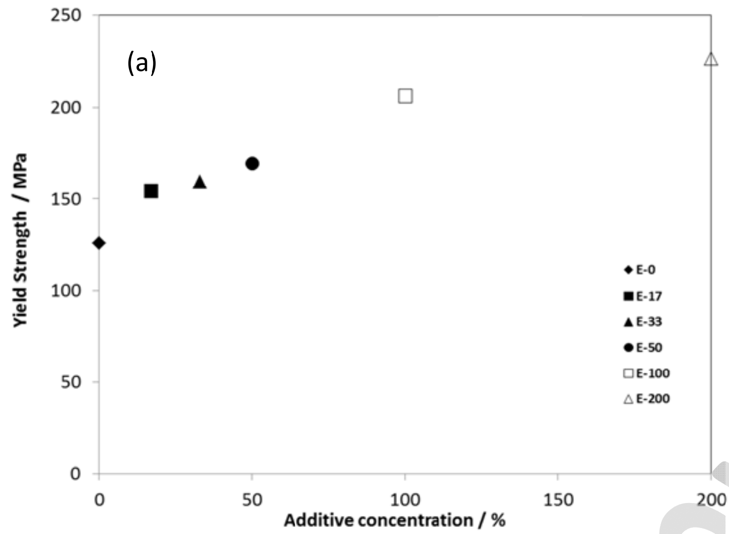

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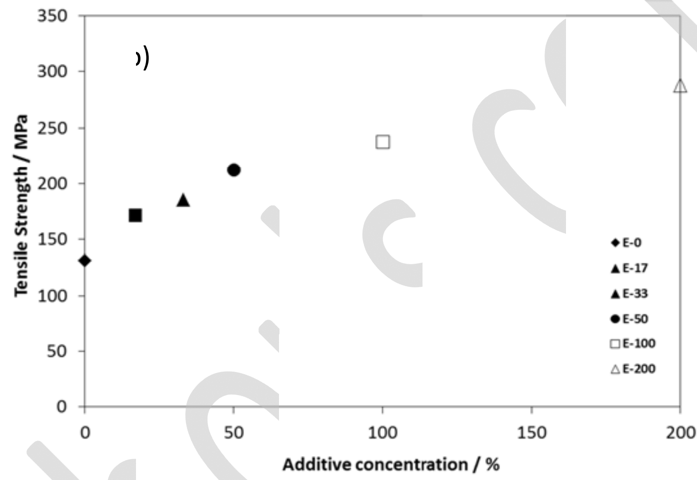

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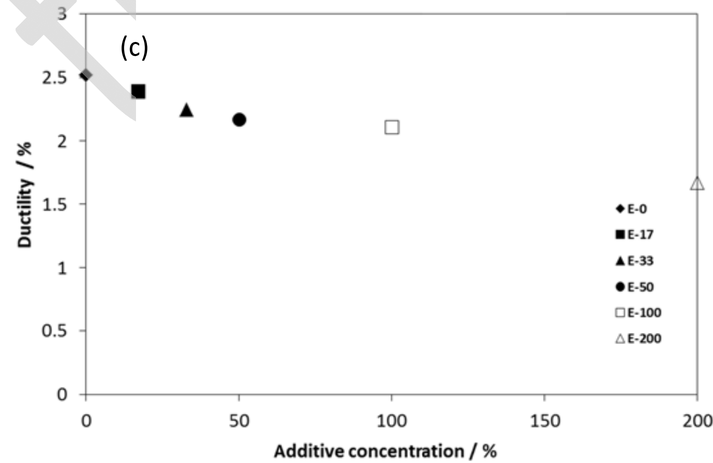

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457 **Figure 4: The a) yield strength, b) tensile strength and ductility of plated copper films**

458 **using EnFACE electrolyte with varying additive concentrations.**