COPPER ELECTRODEPOSITION FOR ON-CHIP INTERCONNECTION THE ROLE OF DIFFERENT ADDITIVES

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ABSTRACT

Copper electrodeposition from a standard acid bath and a pH 3 electrolyte was studied. The effects of chloride and organic additives on transient and steady state electrokinetic behaviour at the electrode and on structure and morphology of the copper layers were examined. Chlorides play the role of a cathodic stabilising factor, promote epitaxy and possibly levelling. Organic addition agents exert specific effects, which may undergo substantial changes in the presence of other additives. The surfactant component shows the strongest action on copper electrodeposition, strongly affecting both the kinetics of copper discharge and the growth mode. The main role of brightener and leveller consists in counteracting the strong inhibiting action of the surfactant, giving the best balance of catalysing and suppressing factors. The pH 3 electrolyte is shown to be a valuable alternative to the standard acid copper bath.

INTRODUCTION

Copper plating baths for the microelectronic industry contain a multi-component additive system, with a particular formulation to achieve super-filling (1) of sub-micron blind vias and trenches, and sulphuric acid as supporting electrolyte, to provide a high throwing power, that is a good thickness uniformity at wafer scale. An optimised choice of different additives is required, since, besides the action of the single additive, their synergetic effect produces the desired balance of inhibiting and accelerating actions (2), particularly in connection with the topographic features of the substrate. However, the complex behaviour of additives mixture is the main reason why it is still not possible to draw a clear picture of their functioning and their selection is still largely founded on the empirical observation of their effects.

The standard bath for copper plating on wafer for interconnection is an acid, low copper concentration electrolyte. Landau (3) has recently proposed a novel “no-acid” sulphate bath with a much higher copper concentration. This electrolyte promises a number of beneficial effects with regard to both thickness uniformity and gap–filling capability, as pointed out by Landau.

In this work the role of an additives set, taken as generally representative of the addition agents regularly employed in copper plating baths, is studied by means of a transient technique, the Secondary Current Pulse (SCP) technique (4), in the attempt to give an interpretation of their action, in both the standard and novel electrolyte. The additives influence on structure, morphology and roughness (5) of copper deposited onto silicon substrate, coated with a 100 nm Cu sputtered seed layer, are considered in the light of these results.

EXPERIMENTAL

The deposition was carried out from both a 0.25 M $CuSO_4$, 1.5 M H_2SO_4 standard electrolyte and a 0.8 M $CuSO_4$ electrolyte at pH 3. Plating baths were prepared from chemicals of analytical grade and distilled water; pH was adjusted with dilute sulphuric acid, when needed. Chloride traces in the original solutions were precipitated by small addition of silver carbonate (1mmol/l). After standing overnight, the solution was filtered, treated with active charcoal and electrolysed at low current density (cd, <0.5mA/cm^2) for about 24 hours.
The effect of four additives, namely Cl^- 50 ppm, dibenzyl–dithio–carbamate (TC) 8 ppm, MW 1500 polyethylene glycol (PEG) 300 ppm and a quaternary ammonium salt (QAS) 18 ppm, was studied. Table I lists plating bath compositions. After additives addition, a further low cd treatment (1 mA/cm^2) was carried out on solutions N and Q, while the other solutions were worked at the standard cd of 20 mA/cm^2 until a sound copper layer was obtained. This was not possible when depositing from stirred solutions containing a single additive component, namely in the case of bath L and, to a lesser extent, bath G, due to the strong inhibition on copper electrodeposition.

Table I: Copper plating baths composition.

Solution	**$CuSO_4 \cdot 5H_2O$ mol/l**	**H_2SO_4 mol/l**	**Cl^- ppm**	**1500MW PEG ppm**	**TC ppm**	**QAS ppm**
A	0.8	to pH 3	---	---	---	---
A1	0.8	0.5	---	---	---	---
B	0.8	to pH 3	50	---	---	---
B1	0.8	0.5	50	---	---	---
C	0.8	to pH 3	--	300	---	---
E	0.8	to pH 3	50	---	8	---
G	0.8	to pH 3	50	300	---	---
H	0.8	to pH 3	50	300	8	---
L	0.8	to pH 3	50	---	---	18
N	0.8	to pH 3	50	300	8	18
F	0.25	1.5	50	---	---	---
J	0.25	1.5	50	300	---	---
Q	0.25	1.5	50	300	8	18

Silicon coated with a titanium nitride/copper stack was used as substrate throughout this work. The sputtered copper layer was 100 nm thick and [111] textured. The counter electrode was an electrolytic copper plate of large area. Electrodeposition was carried out in prismatic Pyrex cells containing 300 ml of electrolyte.

Deposits were characterised by X–ray diffraction (XRD), with CuKα radiation and a powder goniometer, Scanning Electron Microscopy (SEM) and laser micro–profilometry. Microroughness data are given as R_a, R_p and R_{max} measurements for flat Cu sputtered Si substrate: R_a is the arithmetic average of the absolute value of all points of the profile, also referred to as centre line average height; R_p is the maximum distance between the highest profile point and the mean line of the profile; R_{max} is the maximum peak to valley height. Copper layers for structural and morphological examination, as well as microroughness measurements, were deposited from solutions de-aerated by nitrogen bubbling before plating, under magnetic stirring and operated at 20 mA/cm^2; the temperature was maintained at 25°C. The influence of additives addition on the electrokinetic behaviour of the plating baths was studied by steady state and transient electrochemical techniques.
Low scan linear sweep voltammograms were performed after deposition of a thin copper layer (20 mA/cm^2, 10 min) on Si/TiN/Cu(100nm) substrate, with a cathodic area of 0.15 cm^2 from de-aerated solutions at 25°C and under magnetic stirring. The potential was driven in the cathodic direction at a scan rate of 0.2 mV/s from the open circuit potential up to an end current of about 50 mA/cm^2. The Ag/AgCl reference electrode was placed at about 5 mm from the working electrode; the recorded polarisation curves were not corrected for uncompensated ohmic resistance. At the peak current corresponding to 50 mA/cm^2, the ohmic drop was about 25 mV, for the pH 3 electrolytes, and 5 mV for the acid baths.
Transient galvanostatic experiments were carried out in de-aerated solutions, without stirring, at 30°C, with a standard three–electrode configuration and a platinum reference electrode, over–imposing short (4 ms) square current pulses (30, 40, 50 and 70 mA/cm^2) during amperostatic deposition at 20 mA/cm^2. Before measurements, copper was deposited from the bath under study, at 20 mA/cm^2 for 30 min. Ohmic drop in solution, η_ω, could be readily obtained from the transients; a linear relationship between η_ω and $(i_P - i_D)$ was found to hold in all instances.
The overvoltage transient is described with a two terms equation: the first resulting from the equivalent circuit of the potentiometric cell (consisting of the parallel of a non–linear resistor with Tafel characteristic and a variable adsorption pseudo-capacitance); the second from a linearised Sand–type contribution. The following equation of the overpotential transient results:

$$\boldsymbol{h} = B_T \cdot \ln\left[\frac{i_P}{i_D} - \frac{i_P - i_D}{i_D} \cdot \exp\left(-\frac{i_D \cdot t}{B_T \cdot C_{ads}}\right)\right] + \frac{RT}{zF} \cdot \sqrt{\frac{t}{\boldsymbol{t}}} \qquad [1]$$

with parameters: B_T [mV/decade] the transient Tafel slope, C_{ads} [μF/cm^2] the adsorption pseudo-capacitance, τ [ms] the relaxation time; i_D is the deposition cd and i_P the pulse cd. B_T is related to the asymptotic value reached after charging; if a steady state is not

reached at the end of the pulse, when phenomena preceding or parallel to the charge transfer step appear to influence the cathodic process, B_T can be inferred from the time behaviour of the transient, introducing the second term for the overpotential. The capacitance behaviour at the electrodic surface is related to the nature and amount of electroactive species adsorbed at the electrode and the law $C_{ads} \cdot \exp(\eta/B_t) \cdot (d\eta/dt)$ is assumed, taking into account the influence of the surface overpotential η also on the pseudo-capacitance change at the electrodic surface. A linear relationship between $\tau^{1/2}$ and the reciprocal of $(i_P – i_D)$ was observed, while the product of $\tau^{1/2}$ times i_P or $(i_P – i_D)$ was not constant, thus showing that the observed phenomena do not conform to the case of electrode process controlled only by diffusion (6).

In fact, cupric ions diffusion is not likely to affect the transient behaviour at the electrode, within such a short time as 4 ms: the transition time for Cu^{2+}, in the case of the $CuSO_4$ 0.25 M solution and for the experimental conditions employed in this work, can be estimated using the Sand equation

$$\boldsymbol{t}^{1/2} = \frac{nF(\boldsymbol{p}D)^{1/2} C_o}{2i} \qquad [2]$$

τ results to be about 5 s, calculating the diffusion coefficient of Cu^{2+} from the interpolation formula given by Quickenden and Jiang (7), assuming that the high supporting electrolyte concentration has only a small effect on *D*. Moreover, within such time length, convection transport is likely to be effective. In the case of the $CuSO_4$ 0.8 M solution at pH 3, migration effects are expected to be very important and the Sand equation does not hold true; however, the hypothetical transition time τ for Cu^{2+} reduction, calculating the Cu^{2+} diffusion coefficient as above, is about 11 s. Therefore, at the time scale of the transient, the possible overlapping of kinetic and mass–transport effects due to Cu^{2+} diffusion can be definitely excluded.
As to the reduction of Cu^{+}, if stable in the bulk solution, very low transition times results from the Sand equation, about 1.7 ms and 18 ms, for the $CuSO_4$ 0.25 and 0.8 M solutions, respectively, for equilibrium concentrations, corresponding to the maximum thermodynamically stable concentration in the solution, and diffusion coefficient $D = 1.38 \times 10^{-5}$ cm^2/s, given by Tindall and Bruckenstein (8). Thus, in this case, the possible effect of Cu^{+} diffusive transport upon the transient behaviour at the electrode could not be ruled out. However, the observed correlation between the relaxation time τ and the pulse current points to a different behaviour, possibly related to the surface stability of the reacting species. Therefore, for the experimental conditions considered here, it is reasonable to assume diffusive transport as not showing an appreciable influence upon the transient behaviour at the electrode.
In the following discussion, the $t^{1/2}$ term is assumed as representative of relaxation interfacial effects; in principle, this behaviour could be related either to the modification of the surface concentration of discharge intermediates, or to the relaxation of additives surface coverage at the electrode, as a consequence of their diffusion controlled adsorption. However, the former case will depend on the latter; therefore, it will be assumed that the effects observed reflect the relaxation of the surface concentration of cuprous intermediates.

Evidence of strong interaction between cuprous intermediates and electrode surface was given by Wiart *et al.* (9) and by Hurlen (10).
The observation of the transient behaviour at the electrode gives a different viewpoint on the effects of the composition variables upon kinetics and growth; although the SCP method provides a relatively simple picture of the phenomena taking place at the electrode, it enables us to separate surface effects from transport phenomena, focusing on the nature and characteristics of the species reacting at the electrodic surface.

RESULTS AND DISCUSSION

The influence of different additives on potentiodynamic current-potential characteristics and steady state overpotential during copper galvanostatic deposition, was investigated first. Low scan linear sweep voltammograms for the $CuSO_4$ 0.8 M solutions at pH 3 are reported in Fig. 1, showing the influence of chloride and single additive addition on copper electrodeposition. The addition of 50 ppm chloride shifts the curve from about 20 to 40 mV towards higher overpotential, depending on current density; a lower polarisation effect is observed during steady state galvanostatic deposition. This cathodic potential shift in the presence of small addition of chloride was already observed by Chassaing and Wiart (11), depositing from a $CuSO_4$ 1.25 M, H_2SO_4 0.5 M solution. On the contrary, an opposite effect was reported for standard acid cupric sulphate solutions (12); moreover, the catalysing action of chloride ion on the Cu^{++}/Cu^{+} reaction (13) has been recently established. This discrepancy on the polarisation effect of chloride may be attributed to the concentration dependent influence of sulphuric acid, which hinders copper electrodeposition through H_3O^+ adsorption, according to Fukunaka *et al.* (14).

Addition of organic additives involves in any case overpotential increase. The presence of PEG 300 ppm produces the highest cathodic polarisation effect, about 200 mV, both with (bath G) and without (bath C) chloride 50 ppm addition; on the contrary, steady state overpotential was appreciably increased upon addition of chloride (see Table II) in agreement with others (15, 16). For PEG containing solution, the time length for potential relaxation after current interruption is greatly increased, from a few second to several minutes, as a possible consequence of slow additive re-adsorption after the current is switched off. The rest potential shows a cathodic shift of about 30 mV, compared to bath A; upon chloride addition, a further 10 mV cathodic shift is observed, as measured after 5 minutes at open circuit.
The addition of either TC 8 ppm or QAS 18 ppm gives a remarkable polarisation effect; the shape of the curves is affected as well, with a fast current increase at about the same potential, while only QAS causes the slope of the polarisation curve to change appreciably. Steady state overpotential at the deposition cd is substantially higher for bath E, compared to bath L (see Table II). In the presence of QAS (bath L), potential decays almost linearly after current interruption and an equilibrium value is reached very slowly, with about 50 mV cathodic shift with respect to bath B; on the contrary, copper rest potential in bath E remains almost constant, with about 5 mV decrease, compared to bath A or B.

Fig. 2 reports the potentiodynamic curves for bath H, containing PEG 300 ppm and TC 8 ppm, and bath N, containing all additives; potentiodynamic curves for the case of single additive addition are plotted for comparison. In the region of low-medium overpotential, bath H conforms to bath G, due to the overwhelming blocking effect of PEG; at higher overpotential, in the cd range of practical interest for plating, a noticeable depolarising effect due to thiocompound addition is shown, in comparison with bath G, with re-activation at the electrode, as shown by the increased slope of the curve. The overpotential decrease amounts to about 35 mV during galvanostatic deposition at 20 mA/cm^2.
When all additives are present (bath N), the shape of the curve corresponds strictly to that of bath G, thus suggesting that, with regard to the potentiodynamic behaviour of the baths, the leading influence of PEG addition upon the electrode behaviour, although counteracted by the TC presence, is restored by the QAS addition.
Fig. 3 shows the potentiodynamic curves of baths F, J and Q. The addition of PEG 300 ppm to the $CuSO_4$ 0.25 M, $H_2SO_4$1.5 M and Cl^- 50 ppm electrolyte (bath F), strongly inhibits copper deposition, with a potential decrease up to –250 mV. A slightly lower overpotential increase is observed during galvanostatic deposition at 20 mA/cm^2 (see Table II). All additives presence promotes the reactivation of the copper electrode for overpotential above 250 mV, as shown by the sudden current increase. However, steady state overpotential during galvanostatic deposition is higher for bath Q than bath J. This discrepancy can be attributed to an uneven incidence of the concentration polarisation during the potentiodynamic measurements, with enhancement of the mass transport resistance due to PEG and Cl^- combined effect.
Table II summarises the polarisation effect of the different additives, as overpotential increases at deposition cd 20 mA/cm^2, with respect to additives-free baths.

Table II: Overpotential increase, depositing at 20 mA/cm^2, 25°C from stirred solutions, with chloride and additives addition, with respect to additive-free baths A ($CuSO_4$ 0.8M at pH3) and F ($CuSO_4$ 0.25M, H_2SO_4 1.5M, Cl^- 50ppm).

Solution	**A**	**B**	**C**	**E**	**G**	**L**	**H**	**N**	**F**	**J**	**Q**
$\Delta\eta$	0	10	160	90	180	75	150	190	0	230	260
Additives	–	*Cl^-*	**PEG** *no Cl^-*	**TC**	**PEG** *Cl^-*	**QAS**	**PEG + TC**	**PEG+ TC+ QAS**	–	**PEG** *Cl^-*	**PEG+ TC+ QAS**

In the following, the transient electrokinetic behaviour at the electrode in relation to additives addition is examined and discussed, also with reference to structure and morphology of copper electrodeposits (5).
Table III and Table IV list the electrokinetic parameters according to the SCP technique for copper electrodeposition from $CuSO_4$ 0.8 M, pH 3 and $CuSO_4$ 0.25 M, H_2SO_4 1.5 M electrolytes, respectively. The ± variance, reported in the tables, refers to the difference between the average of 6÷12 values, at different pulse current, and the highest and lowest value obtained.

The transient parameters for the pH 3 basic electrolyte (bath A) undergo substantial changes upon Cl^- 50 ppm addition (Fig. 4 shows the overvoltage transient and the curve fitting for both baths): the transient Tafel slope increases from about 45 to 90 mV/dec; the adsorption pseudo-capacitance is reduced to half; the relaxation time τ decreases appreciably as well (see Fig. 5). All these changes point to the important role of chlorides in the cathodic discharge of copper from the pH 3 electrolyte. Chlorides stabilise the discharge intermediate species, lowering the activity of cuprous ions through surface complexation. This effect gives rise to a kinetic hindrance, as shown by the increase of B_T, while, at the same time, activating the surface towards nucleation and growth of new crystals, as inferred from the decrease of both C_{ads} and τ. This interpretation is supported by structural and morphological evidences (5). From bath A, randomly oriented layers are obtained; grain size is relatively large and with poor uniformity; growth features are ill-defined, apart from scattered square base pyramids (Fig. 7). Chloride addition affects structure and morphology: epitaxial growth on the sputtered copper seed layer is favoured and the degree of [111] texture strongly increased (see Table V and Fig. 6); grain size is slightly reduced and more uniform; weak interfacial inhibition gives rise to pyramids with truncated apex (Fig. 7). The observed increase of apparent crystallite size, as obtained by the half height width of (111) reflection according to Debye-Scherrer expression (see Table V), may be related to increased lateral growth. This is also supported by the observation that full-coverage of the substrate occurs earlier than for the chloride free electrolyte, as revealed by AFM imaging of thin copper layers (5), as a consequence of epitaxy through lateral spreading of macro-steps. This is also in agreement with the restoration of singular surfaces and stabilisation of monoatomic terraces observed in the presence of chloride (17), which has been related to the formation of ordered Cl^- overlayers on (111) Cu surface (18, 19).

Chloride effects seem to be almost nullified by the addition of H_2SO_4 0.5 M; the transient behaviour is actually affected by chloride, in the same way as for the pH 3 bath, but the effects are comparatively very weak. Besides, structure and morphology of copper layers from the H_2SO_4 0.5 M baths, with and without added chloride, do not give any support to the above interpretation. This behaviour must be attributed to the strong influence of sulphuric acid in the electrodeposition of copper (14) and suggests that chloride could play a quite different role, as additive, in the “no acid” bath proposed by Landau, apart from its PEG subsidiary action (16).

A noteworthy change caused by H_2SO_4 0.5 M addition (bath A1 and B1) is a well defined plateau for overpotential transients, with disappearance of the relaxation effect accounted for by the second term with parameter τ. Increasing the ratio sulphuric acid to copper sulphate influences the specific adsorption of sulphate anions at the electrode (20) and decreases the Cu^+ equilibrium concentration, as a consequence of the lower cupric ions activity. Since both these factors will lower the Cu^+ surface concentration, this observation supports the assumption that the relaxation time τ can be related to the surface concentration of cuprous intermediates and their stability.

Growth morphology of copper deposits from these electrolytes is characterized by unshaped large grains of poor uniformity; structure develops into a faint [100] preferred orientation, improved by chloride addition.

The transient behaviour at the copper electrode in $CuSO_4$ 0.25 M, H_2SO_4 1.5 M and Cl^- 50 ppm (bath F) is characterised by the following average parameters: B_T 90 mV/dec and C_{ads} 110 μF/cm^2. Values of the relaxation time τ are much higher than in the case of bath B, supporting τ parameter uncorrelation with transport hindrance, a lower surface concentration of reacting species being present in this case. A lower concentration of adsorbed intermediates seems to be present at the surface, when the steady growth of existing crystals is favoured. This is also supported by literature evidence (12); cyclic voltammetry in acid sulphate electrolyte at ring–disk electrode showed that only trace amounts of Cu^+ were formed during deposition. With regard to morphology and structure of copper deposits from this electrolyte (5), high sulphuric acid and low copper concentration promote the growth of weakly textured [100] layers with rounded off pyramidal grains, up to 5 μm in size, in agreement with previous reports (14).

The additives presence noticeably affects the transient behaviour. The effect of single additive addition to the pH 3 base electrolyte, containing Cl^- 50 ppm, was studied first.

In the presence of the thiocompound (bath E), both B_T and C_{ads} increase; the relaxation time τ is higher and shows a much steeper dependence on the pulse cd. The concurrent increase of the electrokinetic parameters points to a mere inhibiting effect of the thiocompound, in agreement with the results of the potentiodynamic analysis. Adsorption of brightener molecules at the surface is effective in depressing the activity of growth sites, showing no evidence of surface blocking. The higher values of the τ parameter with respect to bath B can be related to lower surface stability of discharging intermediates, suggesting a catalytic action of the thiocompound upon the Cu(I)/Cu(0) reduction step. Structural and morphological evidences may be qualitatively related to this behaviour (5): in the presence of only TC, Debye-Scherrer crystallite size is slightly reduced, as reported in Table V, because of increased three dimensional nucleation, and surface morphology is characterised by grains with twinning. The degree of [111] preferred orientation seems to be unaffected with respect to bath B; however, this texture should be considered also as a growth texture imposed by the additive, rather than a plain consequence of the substrate epitaxial effect.

The electrokinetic behaviour in the presence of only QAS addition is interpreted with the following parameters: B_T 120 mV/dec and C_{ads} 40 μF/cm^2; τ values are slightly lower than for bath B. The low value of the pseudo-capacitance is related to the poisoning effect of the quaternary ammonium salt on copper discharge. In fact, selective blocking of the surface is observed, strongly dependent on stirring. The raising transient overvoltage, accounted for by the $t^{1/2}$ term, is again related to the surface concentration of reacting species; the slightly lower values of the parameter τ are possibly the result of the surface interaction of QAS additive and cuprous intermediates.

In the presence of PEG 300 ppm (bath G), the transient behaviour at the electrode changes drastically (Fig. 8 shows potential transients and their interpretation). The following fitting parameters are found: B_T 160 mV/dec and C_{ads} 28 μF/cm^2; τ values are similar to those of bath B. The high value of the transient Tafel parameter suggests a strong inhibition of copper discharge, as consequence of PEG presence, and is related to cluster growth. In fact, B_T values in the range (2.5-3)RT/F, while B in steady state is consistently lower (2RT/F), were observed for cobalt electrodeposition with mixed structure and attributed to nucleation occurring through cluster interaction with the surface (21).

The very low adsorption pseudo-capacitance is also related to the blocking action of the additive, significantly reducing the available exchange surface and selectively blocking the growth sites of highest activity. This is in qualitative agreement with the structural and morphological effects of PEG addition (5): preferential growth of isolated crystal in the early stage of deposition is completely suppressed; the high inhibition level and supersaturation gives growth under nucleation control and with cluster formation; layer growth and epitaxy are no longer stable, as a consequence of the prevailing adsorption interactions. Therefore, PEG plays a key role in promoting the transition from columnar to equiaxial growth.

Table III: Electrokinetic SCP parameters for copper electrodeposition from 0.8 M $CuSO_4$ electrolytes, at pH 3, i_D 20 mA/cm^2, 30°C, no stirring.

Solution	**Composition**	**B_T mV/dec**	**C_{ads} μF/cm^2**	**τ ms**
A	$CuSO_4$ 0.8 M – pH 3	45±15	195±15	17÷0.3
A1	$CuSO_4$ 0.8 M - H_2SO_4 0.5 M	50±5	85±15	--
B	A + Cl^- 50 ppm	90±15	90±10	8÷0.2
B1	A1 + Cl^- 50 ppm	60±10	80±15	--
E	B + TC 8 ppm	100±20	105±5	78÷0.3
L	B + QAS 18 ppm	120±10	40±5	6÷0.35
G	B + PEG 300 ppm	160±10	28±2	7÷0.3
H	B + TC 8 ppm + PEG 300 ppm	140±5	35±5	9.7÷0.3
N	B + TC 8 ppm + PEG 300 ppm + QAS 18 ppm	90±10	34±5	19÷0.6

In the case of the standard electrolyte, the effects of PEG 300 ppm addition (bath J) on the transient behaviour are significantly different from those observed with bath G. The following average parameters are found (see Table IV): B_T 63 mV/dec and C_{ads} 30 μF/cm^2; τ values are much lower than those for bath F, near to those for bath G. This effect of PEG addition agrees with the above assumption of τ being related to Cu^+ surface concentration and stability; in fact, plating additives in acid sulphate bath were shown to increase remarkably the Cu^+ level (12).

Table IV: Electrokinetic SCP parameters for copper electrodeposition from 0.25 M $CuSO_4$, 1.5 M H_2SO_4 electrolytes, at i_D 20 mA/cm^2, 30°C, no stirring.

Solution	**Composition**	**B_T mV/dec**	**C_{ads} μF/cm^2**	**τ ms**
F	$CuSO_4$ 0.25 M - H_2SO_4 1.5 M Cl^- 50 ppm	90±10	110±15	110÷11
J	F + PEG 300 ppm	63±5	30±5	7÷1
Q	F + TC 8 ppm + PEG 8 ppm + QAS 18 ppm	65±10	25±5	10.5÷2.5

These results point to a different behaviour of PEG in the standard bath compared to the pH 3 electrolyte. A possible explanation should be searched for in the chemical interactions between PEG, metal ions and anions at the electrodic surface. It was shown that PEG produces a similar inhibiting effect in both electrolytes, with formation of an adsorbed barrier at the electrode; thus, the observed behaviour should be related to the nature of the surface reacting species. In other words, while in the case of the standard electrolyte the adsorbed barrier layer at the electrode surface is merely a mechanical hindrance towards copper ions transport, in the case of the pH 3 electrolyte it shows peculiar chemical interactions, as revealed by the strong increase of the transient Tafel parameter. Stable complexes formation between PEG and cuprous ions was already envisaged by Hill and Rogers (15), likewise to the case of cyclic polyether complexes with metal salts (22); thus, it is possible to suggest the formation of surface complexes as molecular adducts between copper cations and PEG, acting as electron pair donor with its oxygen atoms. The complex formation could be favoured by both the higher copper concentration and pH, as possible consequence of slightly weaker cation–solvent or PEG–solvent interactions. The strong effect of PEG on the electrokinetic behaviour is followed by structure and morphology changes as well (5). A featureless surface structure develops, due to the strong blocking effect of this additive; the [111] preferred orientation is weakened by all additives, as shown from results of Table V, but the observed dispersion effect appears a special consequence of PEG addition. Debye-Scherrer crystallite size is also strongly affected and, once again, PEG exerts the most relevant influence.

The combined effect of PEG and TC in bath H has a significant influence on the transient behaviour. The following average parameters are found: B_T 140 mV/dec and C_{ads} 35 $\mu F/cm^2$; τ values are slightly higher than for bath G and much lower than for bath E, apart from the value at the maximum pulse cd. Both the decrease of the transient parameter and the low increase of the pseudo-capacitance show that thiocompound addition to bath G promotes a slight activation of the surface, still under the predominant influence of PEG. Such a mitigating effect of thiocompound on the suppressing action of the surfactant was already reported (23) and explained according to a model of "local perforation" of the surfactant adsorbed barrier (2).

When all three additives are present, B_T value is 90 mV/dec and C_{ads} 34 $\mu F/cm^2$; τ values increase (see Fig. 5). The surface conditions are changed towards a lower inhibition level, as shown by both the transient Tafel parameter and the adsorption capacitance changes; the relaxation effect at the surface is slightly restrained, as a consequence of adsorption of both TC and QAS. Structure and morphology do not show any appreciable change with respect to copper deposits from bath H (5): crystal size is slightly increased and the surface shows growth features of high uniformity with the typical equiaxed fine grained structure, as reported in Fig. 10.

In the case of the standard electrolyte, the presence of all three additives causes the transient behaviour to change slightly, compared to bath J, with a further decrease of the adsorption pseudo-capacitance and a small increase of the relaxation time τ, while B_T is almost unchanged.

Table V: Texture and apparent crystallite size of copper coatings on Si/TiN/Cu (25°C, 20 mA/cm^2, stirring, 10 μm). Values of I(111)/I(200) ratio and apparent crystal size are minimum and average values, respectively, observed in 2-4 measurements after 48 h self-annealing.

Plating Solution	A	B	G	E	L	H	N	F	J	Q
XRD I_{111}/I_{200}	1.8	8.0	3.5	8.0	4.5	4.0	4.0	1.0	4.0	3.5
Apparent Crystallite Size (nm)	85	95	50	85	70	55	55	100	60	55

Microroughness measurements of copper films on Si/TiN/Cu(100nm) are reported in Table VI. With chloride addition to the pH 3, $CuSO_4$ 0.8 M electrolyte, surface roughness is almost unaffected, whilst, on a brass substrate Cl^- addition was shown to improve slightly the self-levelling property of the bath (5). It was also reported that low chloride concentration, up to 20 ppm, could promote nodule formation (24), while in this work it was observed the increased tendency of aged solutions to give pitted deposits and worsening of microroughness when pH is slightly increased over 3 (5), in possible relation with Cu_2O codeposition. Both PEG and TC addition to the base solution promote a levelling action. The opposite influence is observed for QAS addition alone, heavily hindering copper deposition. The synergetic effect of PEG and TC, in bath H, shows the most effective smoothening action, while in the presence of all the additives, microroughness is slightly increased with respect to the latter case. Besides, both TC alone and in combination with PEG produces an improvement of macrothrowing power, in comparison with the base electrolyte. The highest microroughness is found in the case of the additives-free standard electrolyte (bath F); the addition of the three additives to this bath (bath Q) does not reduce microroughness to the same extent as in the case of the pH 3 bath (bath N), while PEG addition gives similar results to those of the pH 3 bath, but with higher uniformity.

Table VI: Microroughness of copper deposited on Si/TiN/Cu: additives effect (stirred solutions, 25°C, 20 mA/cm^2, 10 μm thickness).

	Plating Solution	**R_a μm**	**R_p μm**	**R_{max} μm**
A	*$CuSO_4$ 0.8 M pH 3*	0.28	1.35	2.25
B	*A + Cl^- 50 ppm*	0.30	1.35	2.65
G	*B + PEG 300 ppm*	0.26	3.80	4.90
E	*B + TC 8 ppm*	0.25	0.80	1.75
H	*G + TC 8 ppm*	0.18	1.00	1.50
N	*H + QAS 18 ppm*	0.21	1.25	1.95
F	*$CuSO_4$ 0.25 M H_2SO_4 1.5 M Cl^- 50 ppm*	0.38	1.95	3.30
J	*F + PEG 300 ppm*	0.26	1.15	2.15
Q	*J + TC 8 ppm+ QAS 18 ppm*	0.27	1.10	2.00
Sub	*Si/SiO_2/TiN/Cu*	*0.03*	*0.15*	*0.30*

CONCLUSIONS

The influence of different additives on copper electrodeposition from a pH 3, $CuSO_4$ 0.8 M bath and a standard acid sulphate bath was studied.

The chemical interaction between chlorides and cuprous ions, through weak surface complexation, gives a slight interfacial inhibition, as revealed by the overpotential increase for copper discharge in the presence of chloride ions. Without chlorides, the surface concentration of Cu^{+} should be lower than its equilibrium value, since the Cu^{2+}/Cu^{+} step is rate determining (25). Adding chloride, the concentration of cuprous intermediates at the electrode is slightly increased, since their surface activity is lowered; as a consequence, faster nucleation is observed (in correspondence with a transient Tafel parameter increase and an adsorption pseudo-capacitance decrease), with a slight grain refining effect and promotion of epitaxial growth. The beneficial effect of chloride on epitaxial growth was already reported, in the case of deposition onto single crystals (11, 26). This effect of surface stabilisation of discharge intermediates is also in agreement with the reported chloride catalysing action on the Cu^{++}/Cu^{+} reaction (27).

PEG plays the key role in determining both copper deposits microstructure and the electrokinetic behaviour at the electrode; it shows the strongest effect on nucleation, giving equiaxed, fine-grained deposits and smooth surface structure.
The most widely accepted interpretation of PEG influence on copper electrodeposition is based on its role as a diffusion barrier for both copper ions and the other additive components (2, 16, 28). This work provides some evidence in support of the possibility of metal ions–PEG complexes formation, as already envisaged by Hill and Rogers (15), in the case of the pH 3 bath. In fact, the observed high value of the transient Tafel parameter suggests that copper discharge proceeds directly from complex species, stabilised at the surface by adsorption. On the contrary, there is no evidence of significant copper complexation in the bulk solution, in agreement with others (29). Since a stronger surface interaction between PEG and reacting species is suggested from this result, the action of the surfactant is expected to be more effective in the pH 3 electrolyte than in strongly acidic baths.
Thiocompound effect on structure and morphology is related to its activating action on copper discharge, in the presence of blocking inhibitors as PEG (2). The role of the brightener appears to depend on its ability to selectively displace the suppresser at the electrode and slightly re-activate the surface (23).
In the presence of both PEG and TC, the levelling properties of the bath are significantly improved and the lowest microroughness is obtained. If microroughness is taken as a qualitative index of gap-filling capability, it is also expected a definite improvement of the bath fill properties in the presence of the surfactant and brightener additives. Actually, filling of 1:1 aspect ratio vias was successfully achieved with the bath containing PEG and TC, whilst, as expected, vias filling depositing from bath B was unsuccessful; poor results were also obtained depositing from bath G, containing only chloride and PEG (5).

The quaternary ammonium salt influence depends on its adsorption: a strong inhibiting effect is observed in the absence of other organic additives, severely hindering copper discharge. When PEG and TC are present, it shows a re-activating action, with a possible mechanism of surface displacement of adsorbed additives. Besides its effect on the electrokinetic behaviour, the action of this additive appears to be strongly affected by the flow conditions; still, it is readily and tightly adsorbed at the cathode. With regard to gap-filling properties, this addition could play an important role, since its concentration at the free accessible surface is most effectively controlled by adjusting the fluid flow regime and stabilised by strong adsorption; on the contrary, because of the high sensitivity to fluid flow, its supply at recess areas is strongly hindered.

In copper plating on wafer for interconnection, two main issues must be examined: thickness uniformity at wafer scale and gap-filling capability. With regard to thickness uniformity, by lowering the conductivity of the electrolyte it is possible to minimise the terminal effect due to the resistive seed layer, as pointed out by Landau (3), so improving the uniformity of the copper deposit. As concerns the ability of filling trenches and vias, the relative value of activation and concentration resistance is important (30), since both high copper concentration and low activation resistance at the bottom of the vias are desirable. Thus, besides the well recognised importance of additives concentration and fluid flow control, high copper concentration in the bath is likely to be highly beneficial to via filling, as also stated in recent reports (31, 32).

In fact, in this work it was shown that increasing pH and copper sulphate concentration microroughness decreases, as a consequence of increasing copper discharging species transport number; i.e., lowering of the concentration polarisation shows a beneficial effect on deposit micro-distribution. The improved levelling properties of the bath are present also in the absence of additives; it could be interesting to investigate the possibility of decreasing the additive load of the bath, even with elimination of some component of the additive system. Further work is needed to better understand the plating ability of the bath and the properties of the deposits.

In conclusion, the pH 3 copper sulphate bath was shown to give results comparable and even better than those obtained from a standard acid copper sulphate bath; these findings support Landau’s views, making it an attractive alternative to the standard acid bath for plating onto wafers.

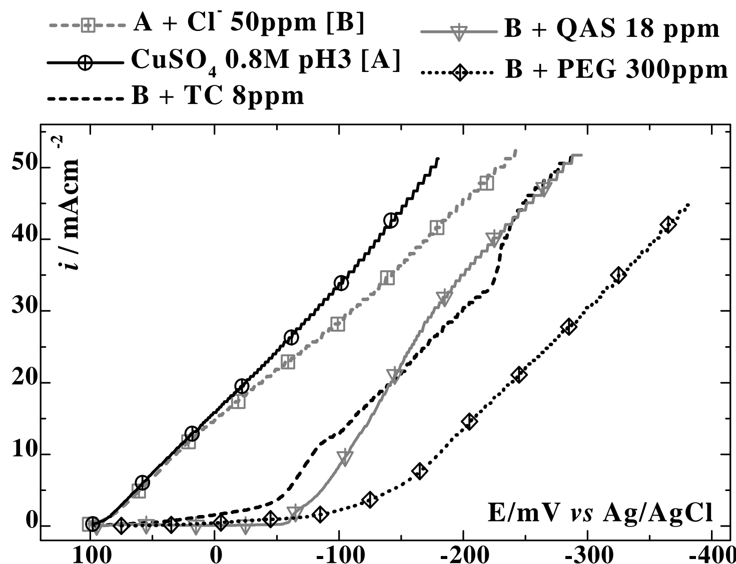

Fig. 1: Potentiodynamic curves for the electrodeposition of copper from $CuSO_4$ 0.8M, pH 3, at 25°C, under magnetic stirring.

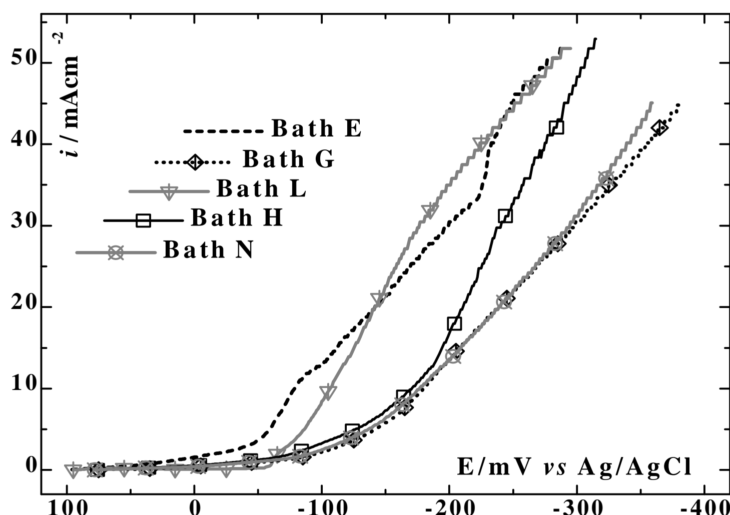

Fig. 2: Potentiodynamic curves for the electrodeposition of copper from $CuSO_4$ 0.8M, Cl^- 50ppm, pH 3, in the presence of additives (E, TC addition; G, PEG; L, QAS; H, PEG+TC; N, all additives), at 25°C, under magnetic stirring.

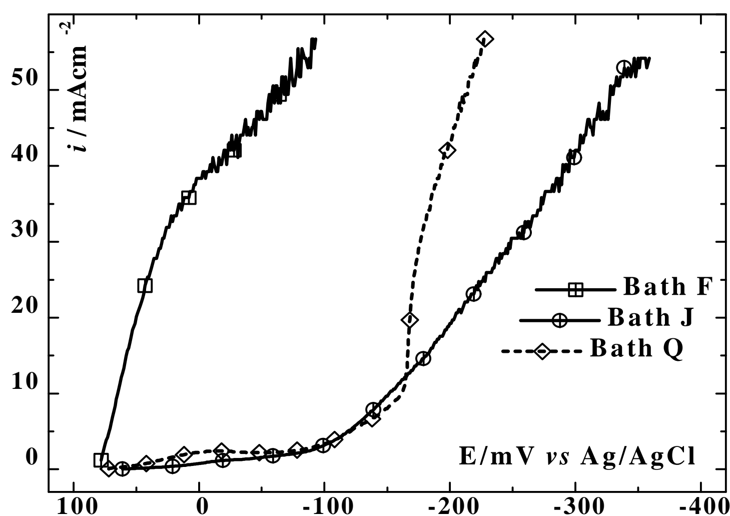

Fig. 3: Potentiodynamic curves for the electrodeposition of copper from $CuSO_4$ 0.25M, H_2SO_4 1.5M, Cl^- 50ppm (bath F; + PEG, bath J; all additives, bath Q), at 25°C, under magnetic stirring.

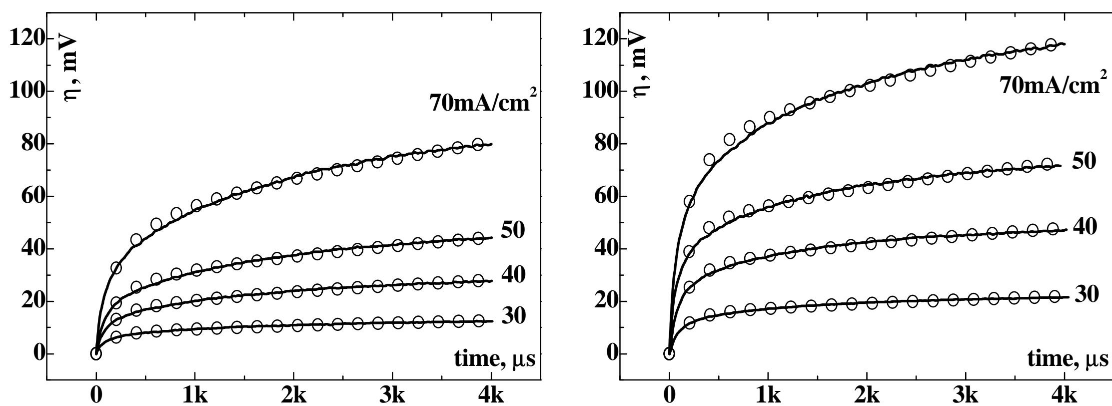

Fig. 4: Transient overvoltages (straight line) and SCP fitting curves (scatter line) for electrodeposited copper at 20 mA/cm^2, 30°C, no stirring, from 0.8 M $CuSO_4$ at pH 3 (left) and after 50 ppm Cl^- addition (right).

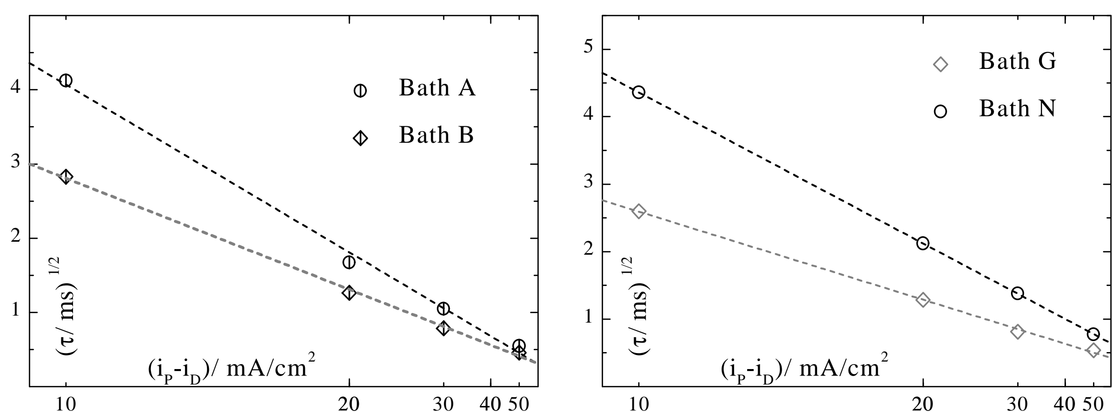

Fig. 5: Relaxation time τ *vs* the reciprocal of the current density i_P-i_D for electrodeposited copper at 20 mA/cm^2, 30°C, no stirring, from bath A and B (left) and bath G and N (right).

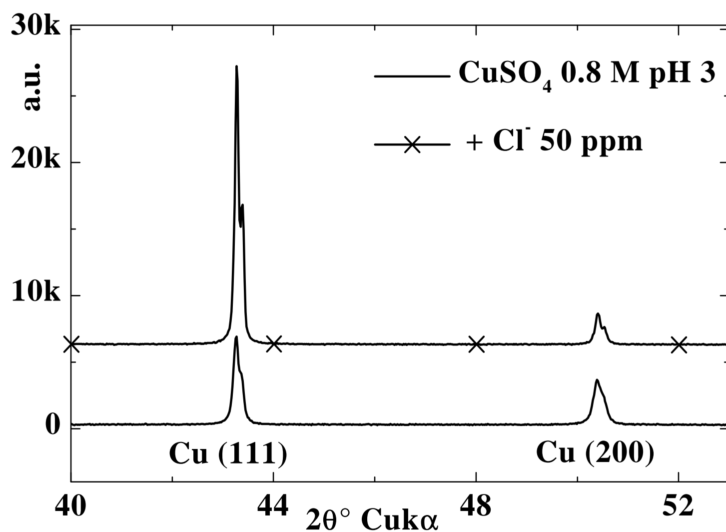

Fig. 6: X-ray patterns of copper deposits from $CuSO_4$ 0.8M, with and without Cl^- 50ppm, at 20 mA/cm^2, 25°C, under magnetic stirring.

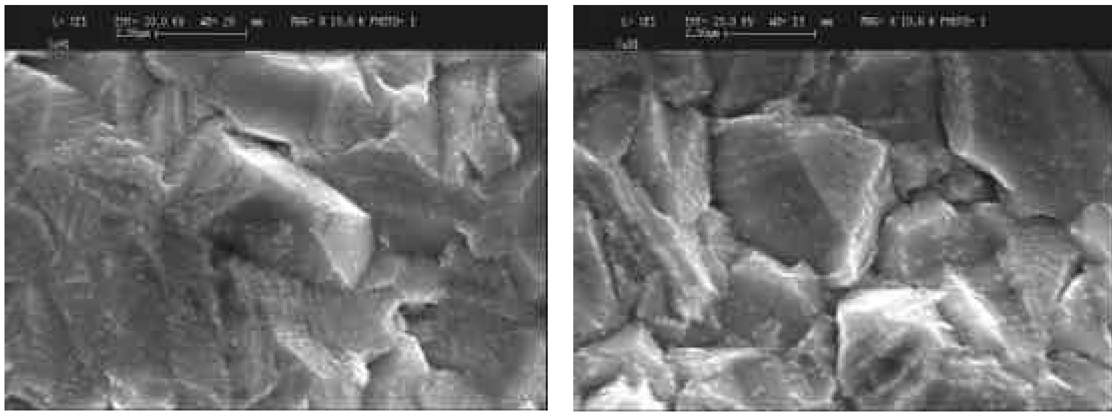

Fig. 7: Growth features of copper films on brass from bath A (left) and B (right); 30°C, 20 mA/cm^2, stagnant electrolyte.

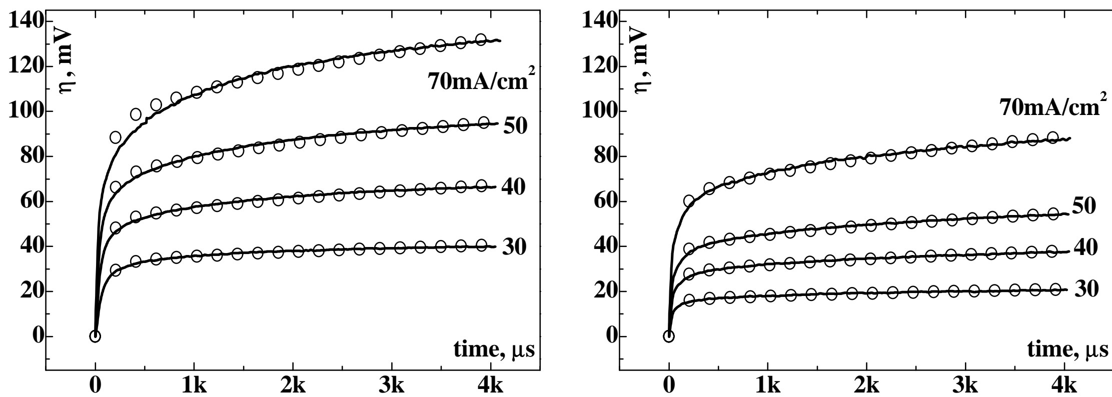

Fig. 8: Transient overvoltages (straight line) and SCP fitting curves (scatter line) for electrodeposited copper at 20 mA/cm^2, 30°C, no stirring, from bath G (left) and bath N (right).

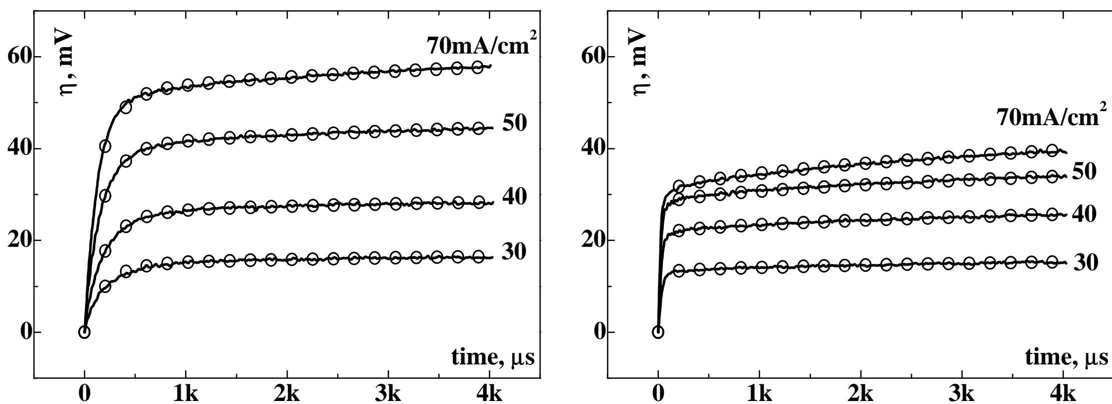

Fig. 9: Transient overvoltages (straight line) and SCP fitting curves (scatter line) for electrodeposited copper at 20 mA/cm^2, 30°C, low stirring, from bath F (left) and bath Q (right).

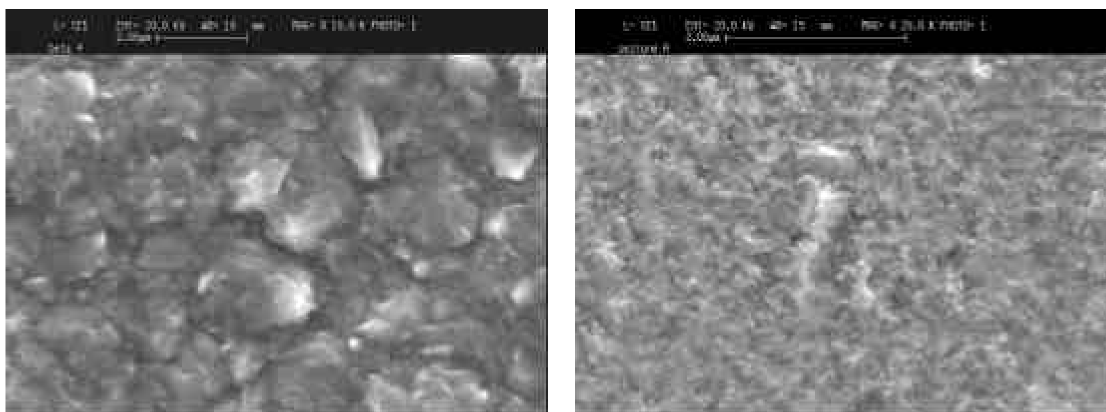

Fig. 10: Surface (left) and cross section (right) morphology of copper deposited from bath N; 25°C, 20 mA/cm^2, magnetic stirring.

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