Copper Microelectrodeposition
The Influence of Different Additives on Growth in Microprofiles

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Acid copper sulfate bath is the standard electrolyte for copper plating on wafers for interconnections. In the present work a pH 3, 0.8 M copper sulfate electrolyte has been used for plating onto both blanket and patterned silicon wafers. This novel electrolyte, recently proposed by U. Landau, involves a number of beneficial effects with respect to the conventional bath.
The influence of four different additives, namely chloride, polyethylene glycol, a thiocompound and a quaternary ammonium salt, on structure, morphology, surface roughness and gap filling properties is investigated. The synergetic effect of additives is discussed with reference to surface roughness and thickness uniformity.

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Introduction

Copper plating baths dedicated to the microelectronic industry contain several additives in order to master the difficult task of filling trenches and vias with the electrodeposited metal[1]. While there is a general and practical understanding of the mechanism of such addition agents, it is still no possible to draw a clear picture of their functioning, although some noteworthy advance has been made[2].

Acid, low copper concentration electrolyte is the standard plating bath for the above mentioned applications. Landau[3] has recently proposed a novel pH 3 sulfate bath with a much higher copper concentration. This electrolyte can offer several advantages with regard to both thickness uniformity and gap–filling capability, as emphasized by Landau.

This work was undertaken to study the feasibility of the novel electrolyte as an alternative to the standard acid sulfate bath and aimed to give a contribution to the understanding of the specific role of a set of additives, which may be taken as generally representative of the kind of addition agents regularly employed in copper plating baths.

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 sulfuric 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 electrolyzed at low current density (cd, <0.5mA/cm^2) for about 24 hours. A further low cd treatment (1mA/cm^2) was carried out after additives addition on solutions N and Q (see Table 1 for composition), while the other solutions were worked at the standard cd of 20mA/cm^2 until a sound copper layer was obtained.

Table 1: 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	---	---	---
F	0.25	1.25	50	---	---	---
G	0.8	to pH 3	50	300	---	---
E	0.8	to pH 3	50	---	8	---
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
Q	0.25	1.25	50	300	8	18

The working electrode was either brass, polished with 0.3 µm alumina, or silicon, coated with a titanium nitride/copper stack. 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. Solutions were de-aerated by nitrogen bubbling before plating; they were not stirred, unless otherwise mentioned, and operated at 20mA/cm^2; the temperature was maintained at 30 or 25°C.

The effect of four additives, namely Cl^- 50 ppm, dibenzyl–dithio–carbammate (TC) 8 ppm, MW 1500 polyethylene glycol (PEG) 300 ppm and quaternary ammonium salt (QAS) 18 ppm, was studied. Table 1 lists plating bath compositions.

Deposits were characterized by X–ray diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and laser micro–profilometry. Microroughness data are given as R_a, R_p and R_{max} measurements, for both polished brass substrate and blanket Cu sputtered silicon substrate: R_a is the arithmetic average of the absolute value of all points of the profile, which is often referred to as center 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.

Results

Chloride and sulfuric acid effect

Electrodeposition from bath A gives randomly oriented layers both on brass and [111] textured thin copper films. Grain size is relatively large and shows poor uniformity (see Figure 1); growth features are not well defined, apart from square base pyramidal grains.

Copper growth from bath A is noticeably affected by 50 ppm chloride addition: grain size is slightly reduced and becomes more uniform (see Figure 1). Chloride seems to exert a weak interfacial inhibition; accordingly, the apex of pyramidal grains becomes truncated. Structure is affected as well: chloride has a strong influence on the degree of [111] texture (see Table 2), enhancing the epitaxial effect of the sputtered copper seed layer; a similar, though less pronounced, improvement of the [111] texture after chloride addition, also results on brass substrate. The degree of the [111] preferred orientation increases raising pH from 2.8 to 3.3, while, regardless of the pH, it is reduced by electrolyte agitation, which on brass substrate actually promotes a slight change towards very faint [110] texture. The observed increase of apparent crystallite size, as deduced by the half height width of (111) reflections according to Debye-Scherrer expression (see Table 2), may be related to the easier lateral growth, a consequence of the low inhibiting action of chloride, which, on the other hand, promotes a small grain size decrease. With regard to the presence of chlorides and cuprous ions, the relatively high pH of the solution may be a point of concern since Cu^{+} is more readily oxidized; furthermore, it may not be disregarded the hydrolysis of cupric ions, which can be also favored by chlorides presence. The chemical equilibria involved may give rise to an aging effect; some evidence of such phenomena has been found in the tendency of the bath to give pits, due to the possible precipitation of insoluble compounds at the copper surface. Such behavior appears to be enhanced when pH is increased above 3.0, while it fades away decreasing pH below 3.0. This behavior is suppressed by addition of additives, at pH 3.0.
Copper films deposited from baths A and B show tendency to easier surface oxidation than copper coatings from standard acid sulfate solution.
No final conclusion may be drawn from these data about the influence of chloride addition to bath A on microroughness, since it seems to be influenced also by the substrate, brass or copper, and by small pH variations. On brass (see Table 3), chloride addition decreases the surface roughness, while on sputtered copper (see Table 5) there is no major change; when the solution pH is raised above 3.0, a strong increase of microroughness results (R_a>0.6μm).

Table 2: Texture and apparent crystallite size of Copper coatings on Si/TiN/Cu.

Plating Solution	XRD I_{111}/I_{200}	Apparent Crystallite Size (nm)
A	2.0÷2.5	85
A1	1.7	95
B	8.3÷9.0	95
B no stirring	5.0	
B – pH3.3	38÷42	100
B – pH3.3 no stirring	9.5	
B1	0.9	95
F	1	100
G	3.6÷4.1	50
E	4.6 [brass]	85
H	3.9÷4.4	55
N	4.0÷5.0	53
Q	3.4÷3.7	55

Table 3: Microroughness of Copper films on Brass; Chloride and Sulfuric Acid influence – 30°C, 20 mA/cm², 10μm thickness.

Plating Solution	R_a μm	R_p μm	R_{max} μm
A	0.41	2.15	4.18
Substrate	*0.15*	*1.86*	
A1	0.58	4.51	5.75
Sub.	*0.28*	*1.18*	
F	0.32	1.57	2.68
Sub.	*0.10*	*0.46*	
B	0.30	1.33	3.03
Sub.	*0.60*	*2.31*	
B1	1.04	5.27	7.67
Sub.	*0.53*	*1.97*	

The addition of H_2SO_4 0.5M to bath A (bath A1) strongly affects the copper growth. The apparent crystallite size increases, along with the grain size, giving easy preferential growth of large grains, while the structure develops into a faint [100] preferred

orientation. Growth morphology is characterized by unshaped large grains with poor uniformity.
Macrothrowing power is noticeably improved, as a consequence of a more uniform primary current distribution, while microroughness for 10 μm thick copper coatings increases. The addition of Cl^- 50ppm (bath B1) gives two major effects: [100] texture improvement and surface roughness worsening.

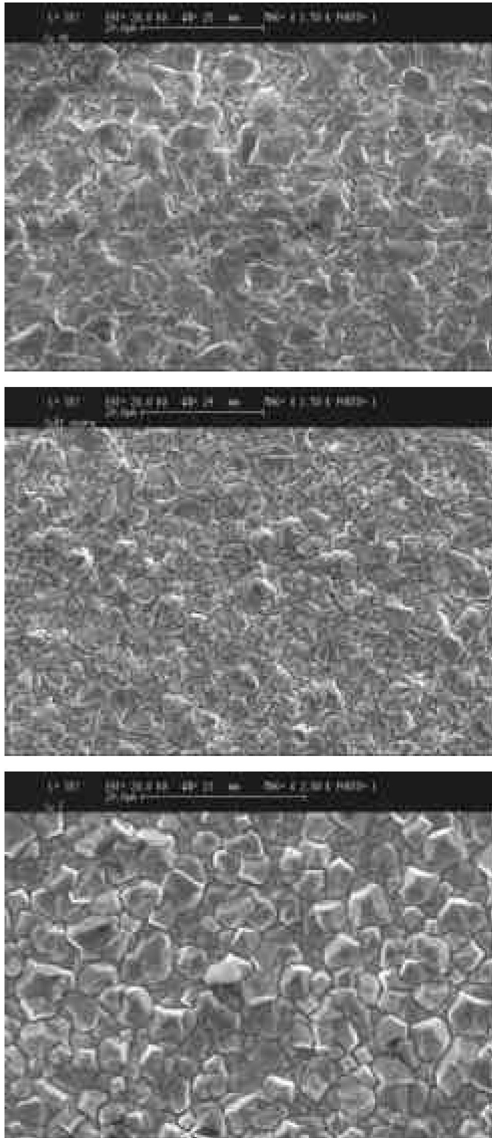


Figure 1: Surface morphology of Copper films from bath A, B and F (from on top downward); 30°C, 20mA/cm2, stagnant electrolyte.

Copper coatings from the standard base electrolyte (bath F) show quite different morphology compared to bath B. High sulfuric acid and low copper concentration promote the growth of rounded off pyramidal grains, up to 5 μm in size (see Figure 1) of improved grain size uniformity. Crystal growth results in a low [100] preferred orientation (see Table 2). Microroughness is slightly increased in comparison with pH 3 base electrolyte (bath B), as shown in Table 3. The high conductivity of bath F has a beneficial effect on thickness uniformity, compared with both bath B and B1 (see Figure 4).

Additives effect

The addition effect of three different additives to the basic pH 3 bath (bath B) was studied. In the case of the standard electrolyte (bath F), only the cumulative effect of the three additives was considered.

As shown from data listed in Table 2, the [111] preferred orientation is weakened by all additives, with regard to bath B: however, the observed dispersion effect appears as special consequence of PEG addition. The degree of the [111] preferred orientation is higher for the pH 3 bath containing the three additives (bath N), compared to the standard electrolyte (bath Q). Debye-Scherrer crystallite size is strongly affected as well, and once again, PEG exerts the most relevant influence; TC addition induces only a small decrease. When the three additives are present (bath N), no appreciable change occurs compared to bath H. Furthermore, apparent crystallite size is only slightly different for deposits from bath N and bath Q. Table 4 lists microroughness results for copper films on brass substrate.

Table 4: Microroughness of Cu films on Brass Additives effect; pH3, 30°C, 20mA/cm^2.

Plating Solution	R_a μm	R_p μm	R_{max} μm
G *	0.21	1.20	1.84
Sub.	*0.19*	*1.26*	
E	0.32	1.17	2.32
Sub.	*0.33*	*1.34*	
L	1.8	7.55	12
Sub.	*0.14*	*0.48*	
H *	0.14	1.14	1.68
Sub.	*0.27*	*1.29*	
N**	0.19	0.74	1.48
Sub.	*0.13*	*1.00*	

* Stirred solution.
** T 25°C.

In the presence of PEG alone, microroughness is appreciably reduced, while TC addition to the base solution does not show improvement. A definitely worsening 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.

Microroughness measurements of copper films on Si/TiN/Cu(100nm) are reported in Table 5. These data, referred to stirred solutions at 25°C, confirm the results of plating on brass substrate, with minor differences: the lowest microroughness is obtained from bath G, while QAS addition induces a slight increase. 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).

Table 5: Microroughness of copper deposited on Si/TiN/Cu: additives effect; stirred solutions, 25°C, 20 mA/cm^2, 10 mm thickness.

	Plating Solution	R_a µm	R_p µm	R_{max} µm
A		0.28	1.35	2.25
B	*A + Cl⁻ 50ppm*	0.30	1.36	2.63
G	*B + PEG 300ppm*	0.26	3.80	4.90
H	*G + TC8ppm*	0.18	1.01	1.50
N	*H + QAS 0.1mM*	0.21	1.25	1.95
F		0.38	1.93	3.29
Q	*F + PEG 300ppm + TC 8ppm + QAS 0.1mM*	0.27	1.12	2.00
Sub	*Si/SiO$_2$/TiN/Cu*	*0.03*	*0.15*	*0.31*

Surface morphology is completely changed by additives addition (see Figure 2). When PEG alone is present, a featureless surface structure develops, apart from undesired growth features due to poor hydrodynamics: this is a clear evidence of the strong blocking effect of this additive. In the presence of TC alone, the surface morphology shows uniform grains, 3 µm or less in size, with macro-twin planes, as revealed by oxide decoration on the surface. Surface morphology of copper films from bath H, which contains both PEG and TC, shows fine roundish crystals, of size down to 200nm, with possible aggregation and cauliflower features.

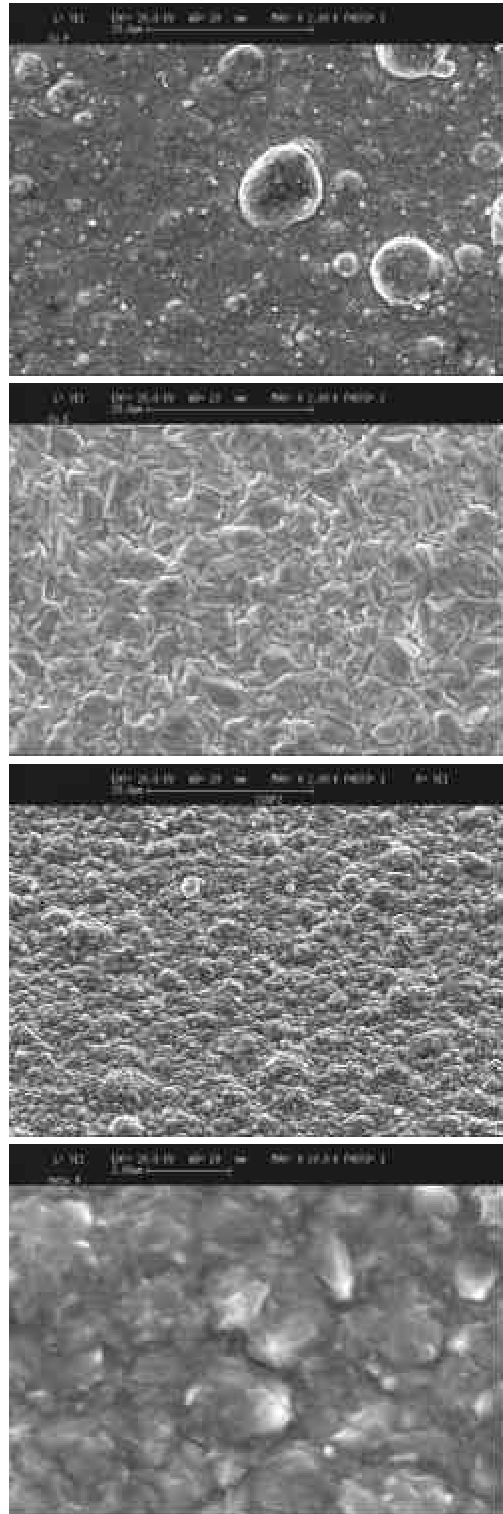


Figure 2: Morphology of copper from bath G, E, H and N (from on top downward); 30°C, 20mA/cm^2, stagnant electrolyte (note different magnification).

These additives show a clear promotion of surface smoothening. Both TC alone and in combination with PEG produces a noticeable improvement of macrothrowing power in comparison with the base electrolyte. The addition of QAS induces a slight grain size increase, up to 1μm; the formation of large aggregates of sharp-edged pyramidal grains is observed when the electrolyte is not stirred.

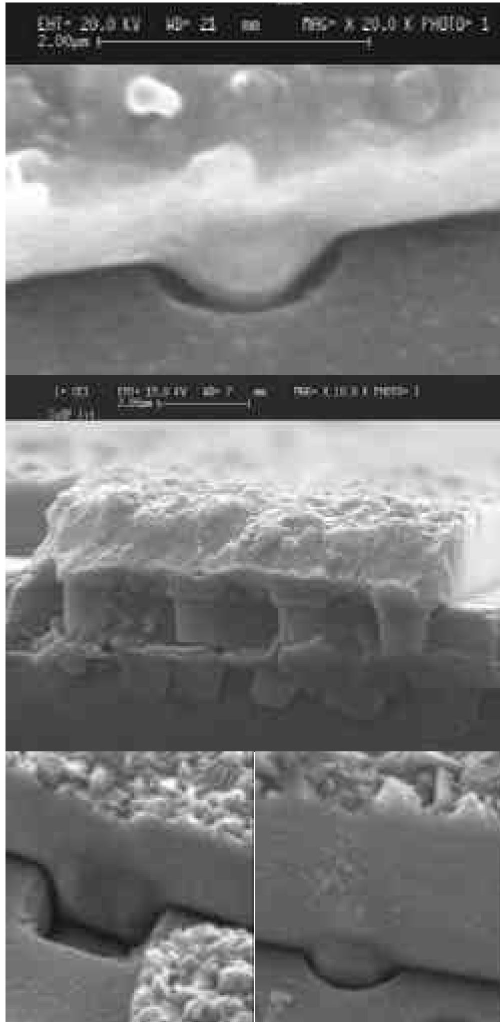


Figure 3: Copper on patterned samples from bath G, H and N (from on top downward).

As expected, the attempt to fill vias depositing from bath B was unsuccessful; poor results were also obtained depositing from bath G (see Figure 3, on top). The electrodeposition on patterned Si/TiN/Cu(100nm) substrate with 1:1 aspect ratio vias from bath H gave good results, thus showing that the two additives, PEG and TC, are needed to give gap-filling capability the base electrolyte. Bath N gave similar results, without significant improvements.

AFM imaging

Surface morphology was also studied during the early stage of copper growth onto Si/TiN/Cu substrate. The following figures presents AFM images of thin copper films electrodeposited from bath B (Figure 5), bath G (Figure 6), bath H (Figure 7) and bath N (Figure 8).

After 30 s deposition from bath B, the copper film shows a surface spotted with relatively large flat or pyramidal crystals, above an underlying layer which consists of roundish particles of less than 100nm size. When chloride are present, full-coverage of the substrate occurs earlier than for the chloride free electrolyte. Thus, chloride promotes nucleation, in agreement with the observed improvement of epitaxial growth. In fact, the latter case involves the lateral spreading of macro-steps, as revealed by the faster full-coverage of the base. Crystal growth from bath B occurs with a fast stage of diffuse nucleation, at the beginning of deposition, and subsequent preferential growth at active sites, possibly in relation with surface defects. PEG addition to bath B completely suppresses the preferential growth of isolated crystal, because of its inhibiting action on the growth sites of highest activity (Figure 6). As a consequence, a surface structure smooth and uniform results; growth control is through adsorption, with epitaxy no longer stable, since discharge sites are strongly reduced.
PEG and TC combined effect causes crystal size to increase, whit growth features not well defined, although from AFM images the formation of twinned crystals can be inferred (Figure 7). The addition of quaternary ammonium salt brings about further changes: crystal size is slightly increased, compared to bath G; the surface shows the most regular structure with growth features of high uniformity.

Conclusions

Structure, morphology and microroughness of electrodeposited copper are affected by electrolyte pH, copper sulfate concentration and 50 ppm Cl^- addition.

- Increasing pH and copper sulfate concentration, microroughness decreases as a consequence of increasing copper discharging species transport number. I.e., lowering of the concentration

polarization shows a beneficial effect on deposit micro-distribution.

- Chloride addition to the pH 3 electrolyte strongly influences copper nucleation and growth: chloride ions, lowering the surface activity of the copper discharge intermediates, act as weak interfacial inhibitors. Promotion of epitaxial growth on [111] texture copper seed layer is observed with surface roughness decrease.
- PEG shows the strongest effect on nucleation, giving very fine-grained deposits and smooth surface structure. Its action requires high hydrodynamic control, since this additive may promote nodular growth.
- Thio-compound effect on structure and morphology is in relation to its activating action on copper discharge. It also exerts the strongest leveling action, improving the macro-throwing power, while surface roughness is almost unaffected.
- In the presence of both PEG and TC, the leveling properties of the bath as well as the macro-throwing power are not further improved. Plating baths containing both PEG and TC give the lowest microroughness on both brass and copper substrates; if microroughness is taken as a qualitative index of gap-filling capability, it is possible to conclude that conformal plating is achieved when both additives are present; in fact, filling of 1:1 aspect ratio vias was successfully achieved.
- The quaternary ammonium salt has a difficult to define influence, depending 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 probably through a mechanism of surface displacement of adsorbed additives. Therefore, its concentration must be carefully adjusted and controlled.

In conclusion, the pH 3 copper sulfate bath was shown to give results at least as good as those obtained from a standard acid copper sulfate bath; these findings support Landau’s views, making it an attractive alternative to the standard acid bath for plating onto wafers.

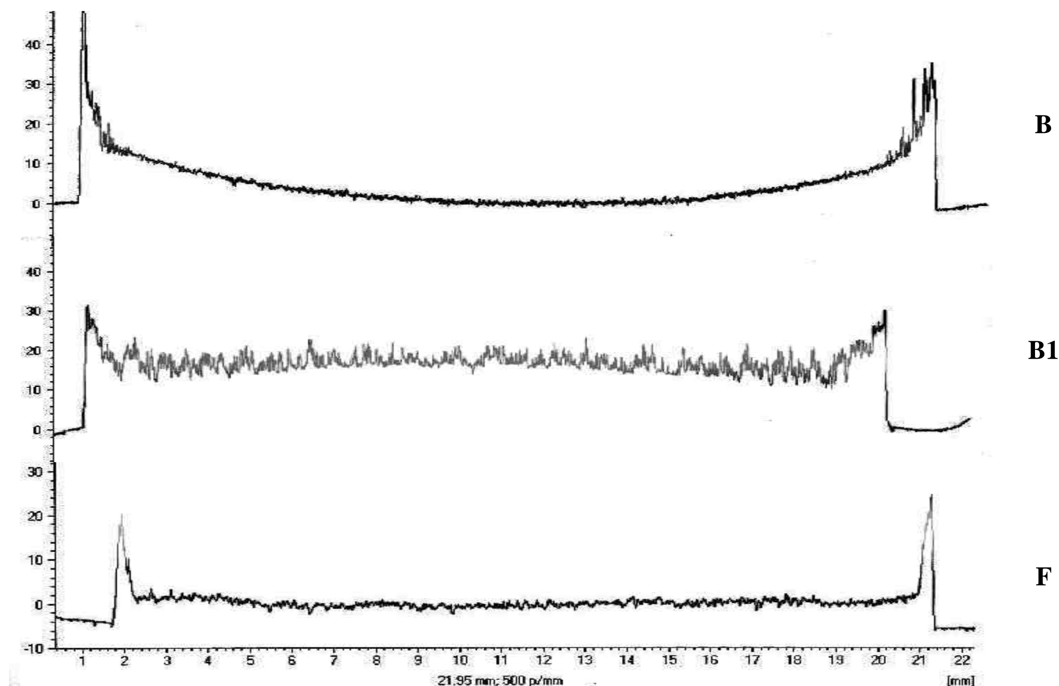
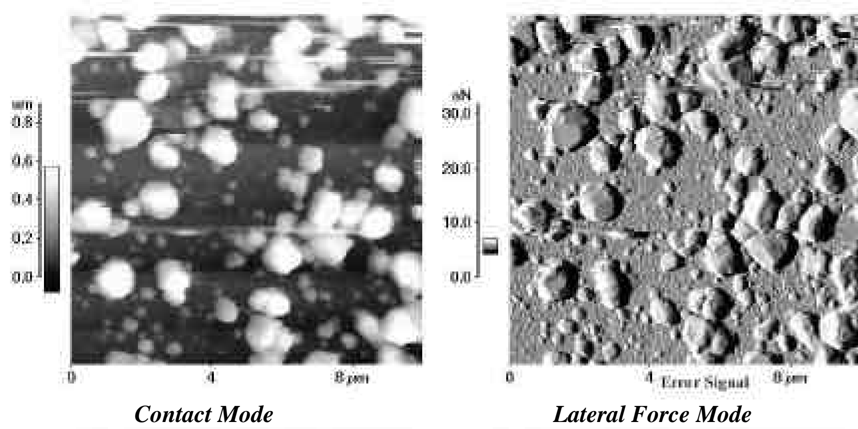


Figure 4: Thickness profile of copper coatings from bath B, bath B1 and bath F, in μm.



Contact Mode *Lateral Force Mode*

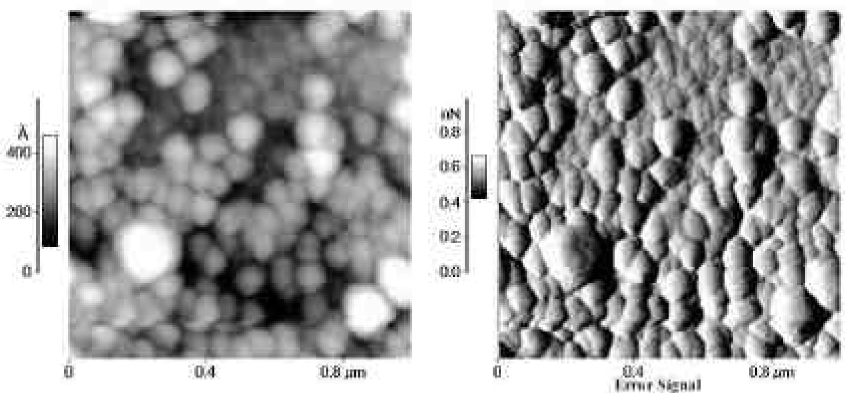
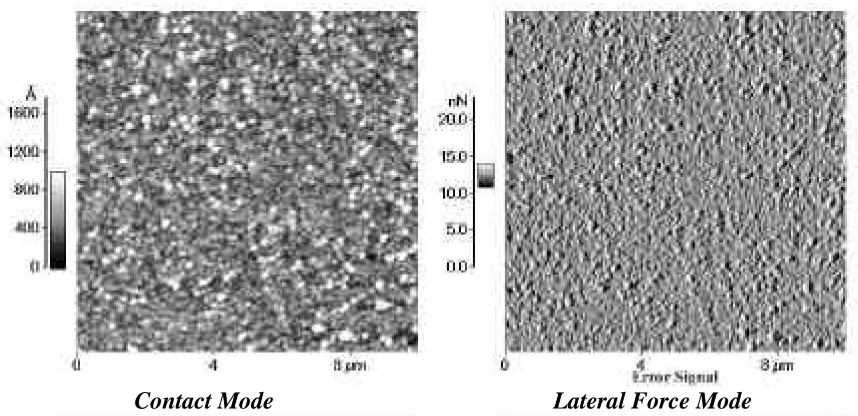


Figure 5: AFM images of copper thin film from bath B, 30°C, 20 mA/cm², 30s, no stirring on Si/TiN/Cu 0.1µm .



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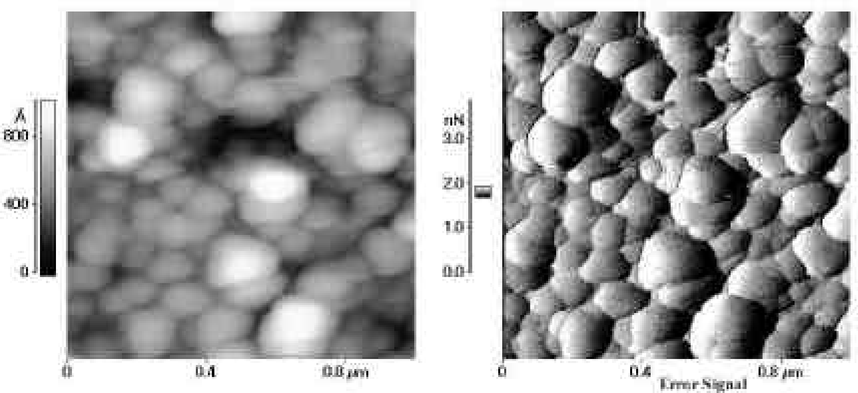
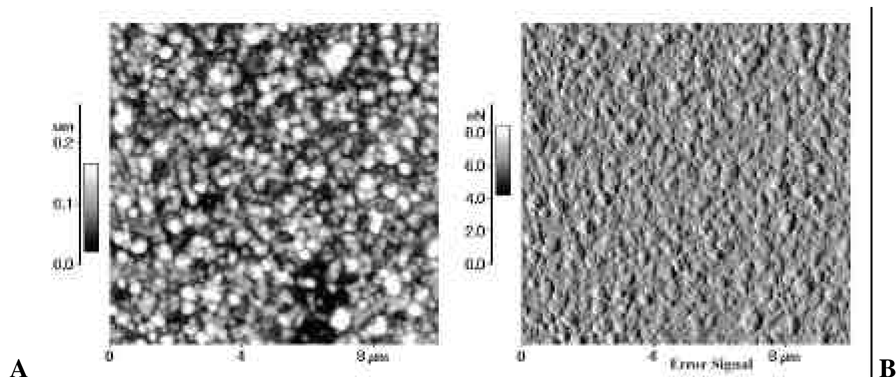


Figure 6: AFM images of copper thin film from bath G; 30°C, 20 mA/cm², 30s, stirring on Si/TiN/Cu 0.1 µm.



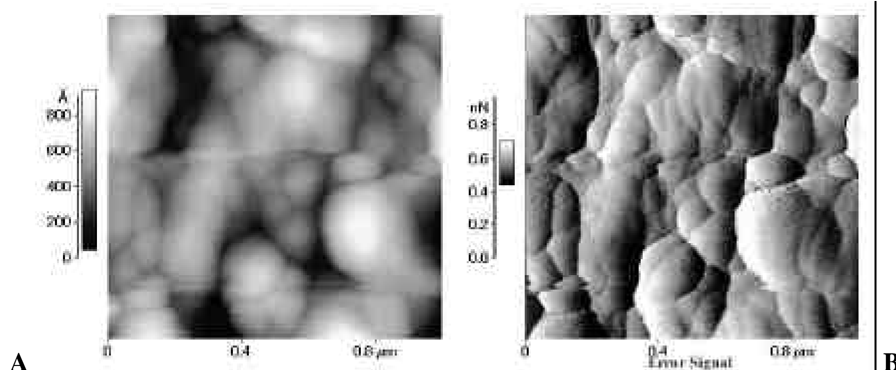
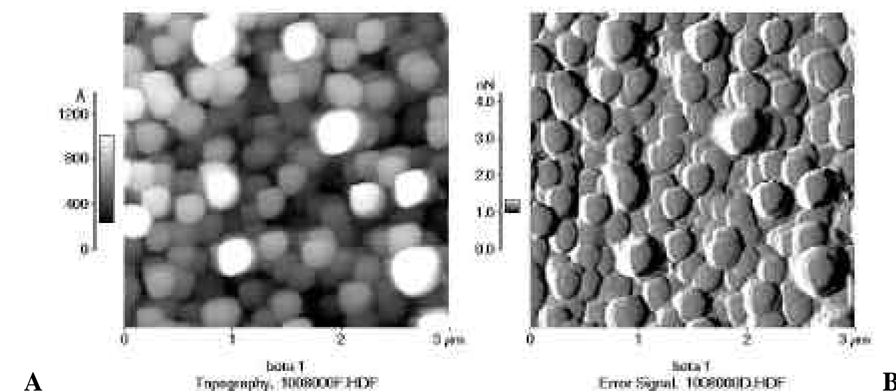


Figure 7: AFM images of copper thin film from bath H; 30°C, 20mA/cm^2, 30s, no stirring on Si/TiN/Cu 0.1μm (A: contact mode; B: lateral force mode).



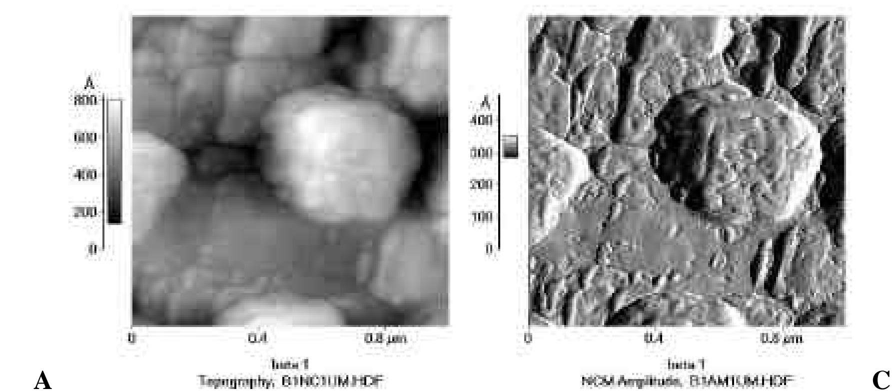


Figure 8: AFM images of copper thin film from bath N; 30°C, 20 mA/cm^2, 30s, no stirring onto Si/SiO$_2$/TiN/Cu 0.1 μm (A: contact mode; B: lateral force mode; C: non contact mode).

References

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