Copper Surface Treatment and Plating Reliability

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Introduction

Reliable copper interconnects are a primary requirement for most printed wiring board applications. A variety of wet manufacturing processes play an important role in the formation of durable interconnects, including plated thru hole (PTH) metallization with electroless copper/electrolytic copper plate. PTH interplane (IP) separation may become an issue when cleanliness and texturing of the IP before electroless deposition is not optimal. Smear removal pretreatment and subsequent processing to provide a clean and properly textured IP before electroless deposition have a strong influence on the resulting roughness and chemical content of the outermost layer of copper surfaces. A method by which to evaluate the surface state of copper during each preclean and chemical processing step would be beneficial to understanding copper surface chemistry, and consequently, some of the origins of IP separation.

The tendency for a metal surface such as copper to undergo electrochemical corrosion can provide some qualitative, as well as limited quantitative information on the relative state of the copper surface after exposure to various corrosive solutions. For example, copper precleaning solutions, including permanganate desmear and acid conditioning, are inherently corrosive and are required in order to generate a properly textured clean surface free of contaminates upon which electroless copper can successfully adhere. The relative corrosivity of the solution the copper is exposed to during preclean will ultimately affect the corrosion rate or corrosion resistance of the surface when exposed to yet another corrosive electrolyte. For example, a relatively corrosive preclean step such as sodium persulfate microetch may leave the copper surface in a more rough, oxidized state than a simple acidified rinse. Consequently, it could be expected that the corrosion rate of this oxidized copper surface would be relatively low in comparison to the corrosion rate of a smooth, pure copper surface afforded by a gentler acid rinse. Because IP separation is a manifestation of poor adhesion between the base copper/ electroless copper or the electroless copper/electrolytic copper interface, a more detailed investigation of the chemical factors that cause changes in copper surfaces can be helpful in understanding the underlying cause(s).

With this objective in mind, a copper clad test vehicle was subjected to desmear and electroless copper plate along with the associated precleans, with a portion of it removed, rinsed and dried after exposure to each individual chemical processing step. The corrosion behavior of each resulting sample surface was electrochemically studied by generating Tafel plots of each surface in 0.3% NaCl electrolyte. Corrosion rates of each unique copper surface after various wet process steps and the corrosion potential of each surface in electrolyte are reported.

Experimental

Electrochemical corrosion testing was performed using an EG&G Princeton Applied Research potentiostat/galvanostat controlled by corresponding M352 software. Saturated calomel (SCE) and Pt gauze were used as reference and counter electrodes, respectively. Tafel plots of the copper surfaces in 3% NaCl electrolyte were generated by applying potential to the test electrode within the range –0.250 to + 0.250 V vs. the rest potential. Each test electrode was immersed in fresh solution with agitation and no potential applied for 1 min to allow the rest potential to stabilize prior to recording polarization curves. All corrosion experiments were run under ambient conditions. All reported corrosion rates represent an average of three individual trials run under the same conditions.

Copper clad laminates were then processed thru a conveyorized Desmear/Electroless Copper tool and removed at various steps within processing to assess corrosivity of the copper just after the step of interest. The steps of interest are outlined in Table 1.

In addition to corrosion testing, Atomic force microscope (AFM) imaging was performed on equal samples from a similar test vehicle on parts treated thru a beaker line using the conditions outlined above. Prior to AFM measurements, each sample surface was electropolished to generate smooth polycrystalline surfaces in order to enhance the grain boundaries and ensure maximum reproducibility. A representative image for each sample type was taken and is included in the discussion.

Table 1 – Wet Process Outline

STEP	DESCRIPTION	DWELL & TEMPERATURE
Sweller	50% v/v butyl carbitol soln.	2 minutes at 75C
Permanganate	60 g/l permanganate	4 minutes at 75C
Neutralizer	10% v/v hydroxylamine soln.	1 minute at 40C
Cleaner	40 ml/l ethanolamine soln.	1 minute at 50C
Conditioner	100 ml/l conditioner soln.	1 minute at 30C
Microetch	120 g/l peroxymonosulfate soln.	1 minute at 35C

Discussion

The process steps studied herein have distinct roles that result in varied copper conditions going into the next step. To provide a very robust interconnect after copper plating, a contaminant-free and properly textured innerlayer is vital. The desmear process (sweller, permanganate, neutralizer) is setup to soften and oxidize the resin material and to dissolve any solid manganese residue from the resin and copper foil surfaces. The neutralizer step also acts as a mild etch, but might not be enough to remove traces of epoxy residue (pseudo smear) especially on the innerlayers. As a result, the copper must be cleaned further to ensure the microetch step is not inhibited by any residues left on the innerlayer. If the microetch step is compromised, the resulting copper texture of the innerlayer could be less than optimal and more susceptible to IP Separation. Therefore the resulting copper corrosivity of the process steps leading up to microetch is of interest and is assessed in both quantitative form with corrosion rates and qualitatively with AFM imaging.

The copper surfaces exposed to the six steps of interest were rinsed, dried, and masked off to create 1 cm^2 electrode area and then exposed to 3% NaCl electrolyte for electrochemical corrosion measurements. Corrosion rates for all samples are shown in Figure 1. The lowest corrosion rates are obtained from samples exposed thru the third desmear step (neutralizer) and microetch. It can be theorized that these solutions leave the copper in an oxidized state and therefore be more passivated towards electrochemical corrosion. The highest corrosion rates are observed for copper processed thru the second desmear step (permanganate) and also thru Cleaner.

Also included in Figure 1, are two different controls. The ‘incoming’ consists of a copper clad sample with ‘as is’ foil that has not gone thru any wet processing. Note that it also has a relatively high corrosion rate, we can attribute this to the absence of foreign traces on the surface of the foil before it undergoes wet processing. On the other hand another control, which consists of a similar sample undergoing Organic Solderability Preservative (OSP) processing, gives another point of reference as to what the copper corrosion rate for such a treatment would yield. Intuitively, it would be best to provide the microetch process step with copper that resembles incoming foil (no organic traces). This would provide for uniform etching, texturing and increased reliability of the interconnect.

During the first two steps of the desmear process, epoxy resin is softened and oxidized which in turn, builds up in the permanganate bath. The copper foil being soaked with such a strong oxidizer could be why such a high corrosivity rate is observed immediately after this step (0.8524 mils/yr). The neutralizer step dissolves the oxidizer remains (in this case, manganese) but it could leave a trace of oxidized resin on copper surfaces originally deposited during the permanganate step. The presence of this pseudo smear could explain why the corrosion rate at this step was one of the lowest (0.2807 mpy).

After desmear processing, two steps of interest (Cleaner and Conditioner) are there to clean copper surfaces further to remove any foreign trace (in this case, oxidized epoxy resin) and to Condition the resin/glass hole wall for optimum seed and electroless copper coverage. This is consistent with the relatively higher rate observed after Cleaner, in which the corrosivity of the copper is at least as good as the incoming copper foil into the wet process. On the other hand, there appears to be some degradation during the Conditioner step as its rate approaches that of an OSP treated copper surface. In many cases, the conditioning is incorporated into the cleaning step or earlier on during the neutralization step in the desmear process. This type of analysis combined with line performance data for both IP Sep and Electroless coverage can be helpful in determining where along the wet process a conditioning step should be placed.

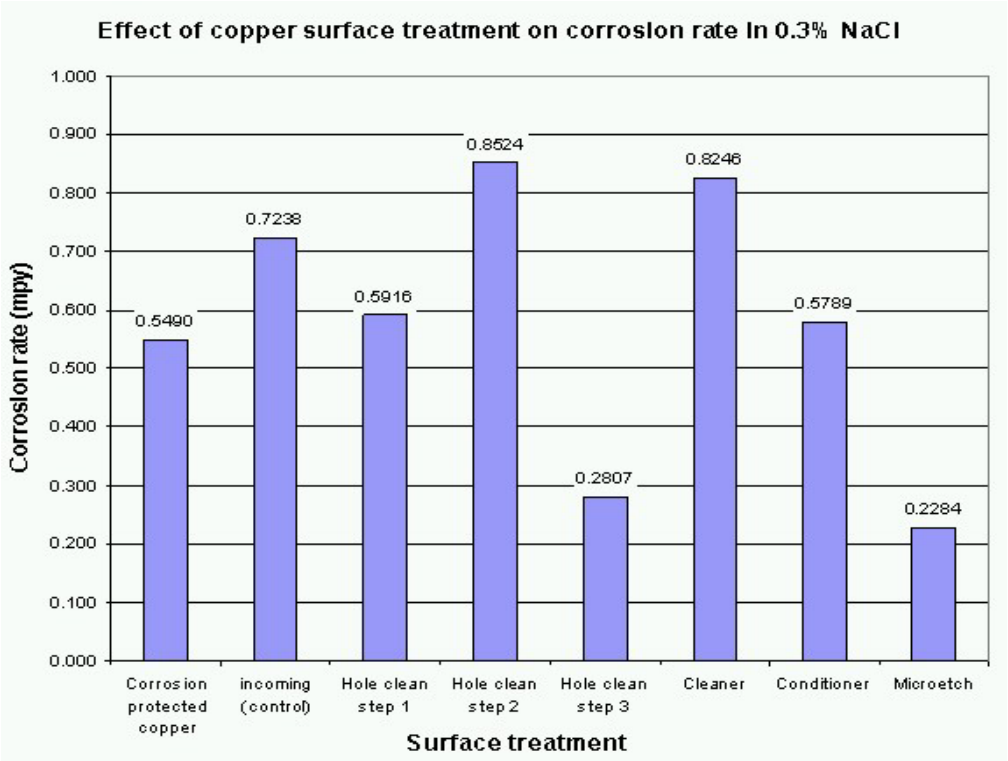

Figure 1 - Electrochemical Corrosion Rates (in mil per year) of Copper Surfaces Exposed to Various Electroless Copper Preclean Process Steps. Data is from the Same Samples Measured in Figure 1. Electrolyte = 3% NaCl; scan rate = 1 mV/sec.

This analysis is also supplemented by corresponding AFM imaging. This can be viewed as a qualitative validation of the corrosion rates yielded by the different wet process steps, assuming that the presence of organic trace inhibits corrosivity of the copper. The imaging shows detail of the crystal grain structure and whether the appearance of the surface changes with the different treatments. Images with a fuzzier surface appearance indicate the presence of trace organics and can result in a less than reliable interconnect, unless this appearance is removed before microetch. This way the etching is uniform and would provide optimized innerlayer texturing to subsequent processing thru electroless copper. In general terms, the goal would be to bring back an appearance similar to that of the incoming foil which was originally free of organic traces or pseudo smear. Following is an image showing the appearance of copper foil before any wet processing:

Figures 2 thru 4 represent the three steps associated with permanganate desmear. Figure 3 shows some level of impurities (stripe) post permanganate processing left on the foil. The surface appearance after neutralizer (Figure 4) though is very distinct from the previous step. At this point, the crystalline structure of the copper foil is very evident some of it due to the slight copper etching that occurs during neutralization. The corrosion rate obtained after the neutralizer step though suggests there might be a trace that limits corrosion to a lower rate than that obtained after the Cleaner step, which visually has a more dramatic appearance per Figure 5. This sharp definition of the crystal structure at this point suggests a surface that is free of organic traces going into the microetch and subsequent wet process leading up to electroless. Again, this is consistent with the corrosion rates obtained after the Cleaner step being higher than the rate after Neutralizer. The Ra value is a measure of the roughness profile, a higher value, indicates a rougher profile. Surface enlargement is percentage of the resulting 3D surface to the planar surface and again, a higher percentage means a rougher profile. These two indices do not necessarily relate to organic trace residues

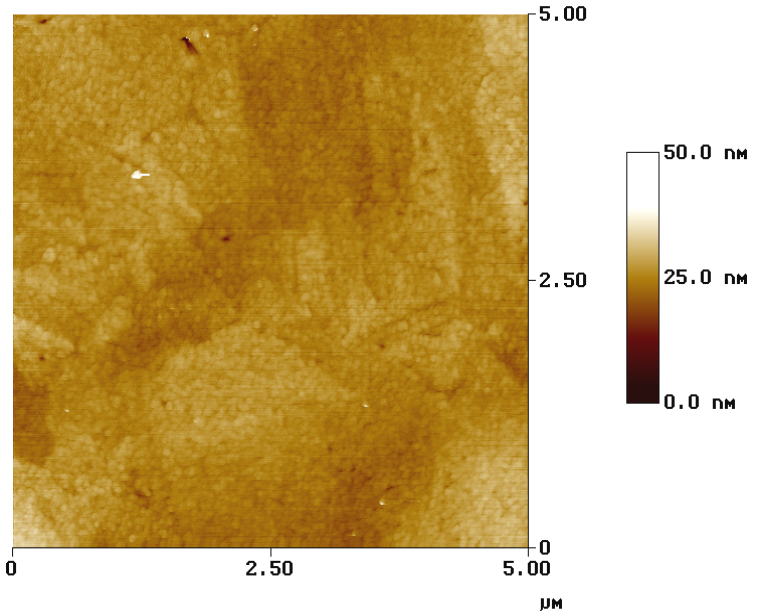

Figure 2 - AFM Images Observed from Copper Surfaces Incoming to the Wet Process

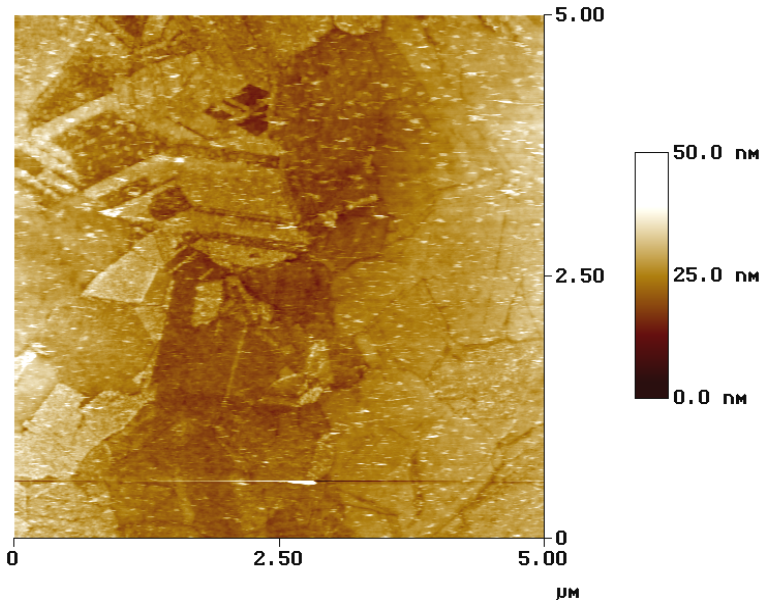

Figure 3 - AFM Images Observed from Copper Surfaces After Sweller and Permanganate

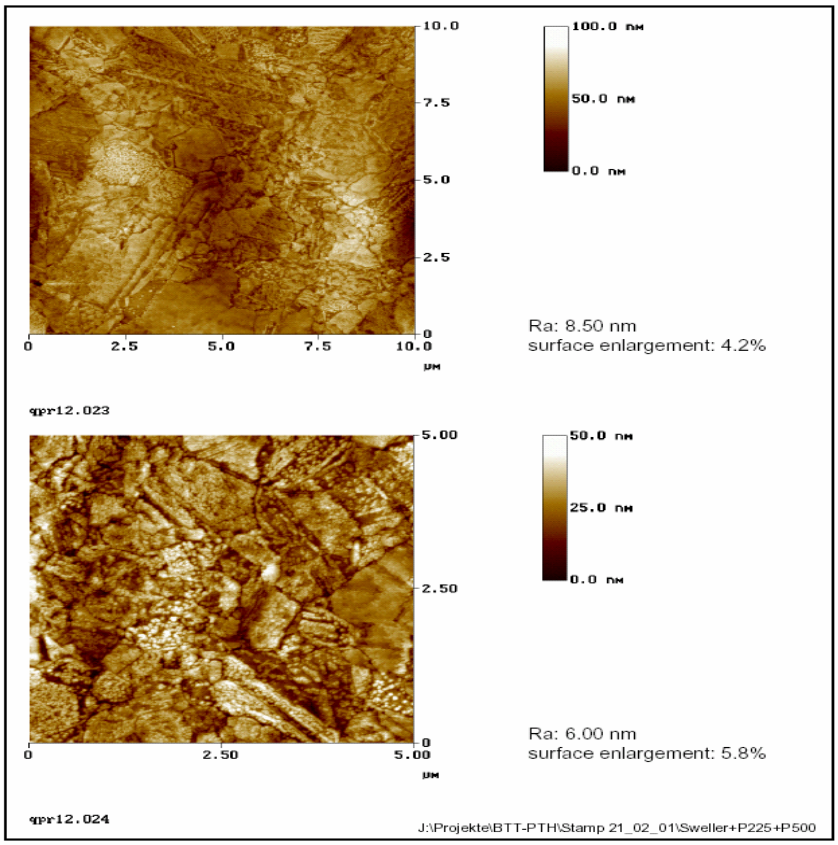

Figure 4 - AFM Images Observed from Copper Surfaces Treated in Sweller, Permanganate and Neutralizer (desmear)

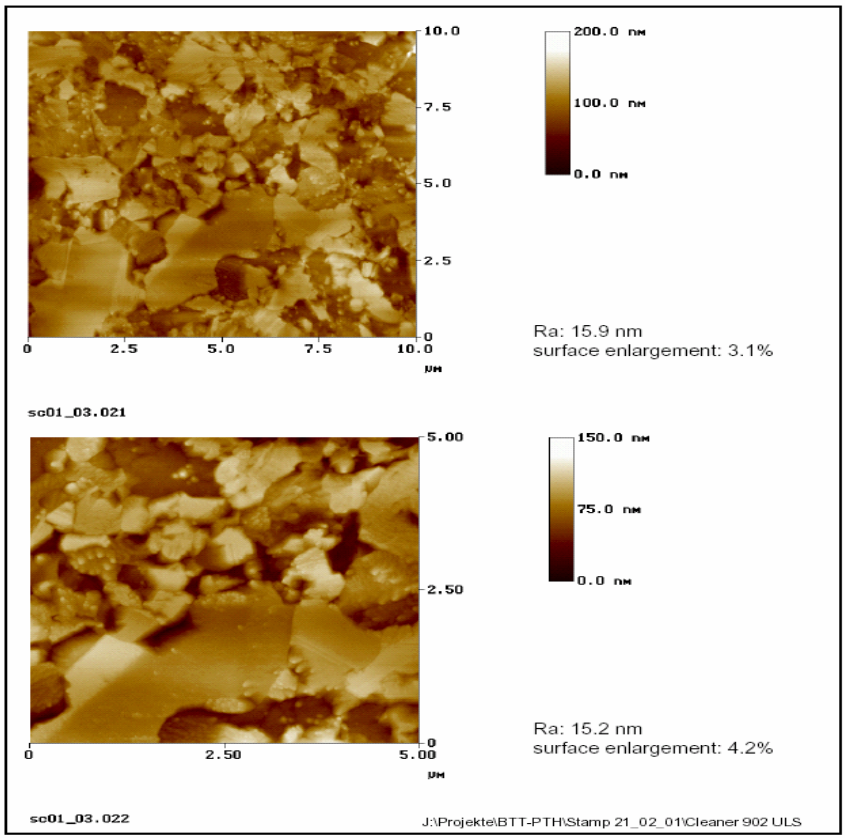

Figure 5 - AFM Images Observed from Copper Surfaces Treated thru Desmear & Cleaner

Conclusion

Results indicate that certain surface treatments cause copper to corrode at lesser rates than pure copper, and good control of these processes may prevent or minimize the chance of IP separation. The results compare favorably to previously obtained Atomic Force Microscopy (AFM) images of copper surfaces exposed to similar chemistry steps. It also validates quantitatively (via corrosion rates) what was originally assessed qualitatively by ranking AFM images for copper cleanliness.

Acknowledgements

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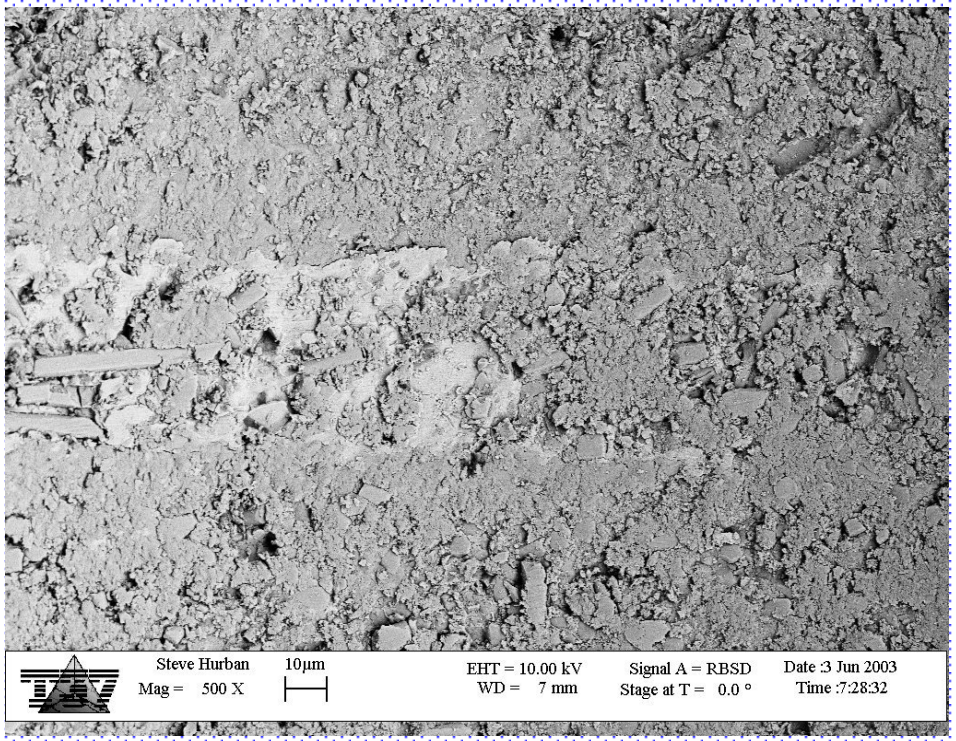
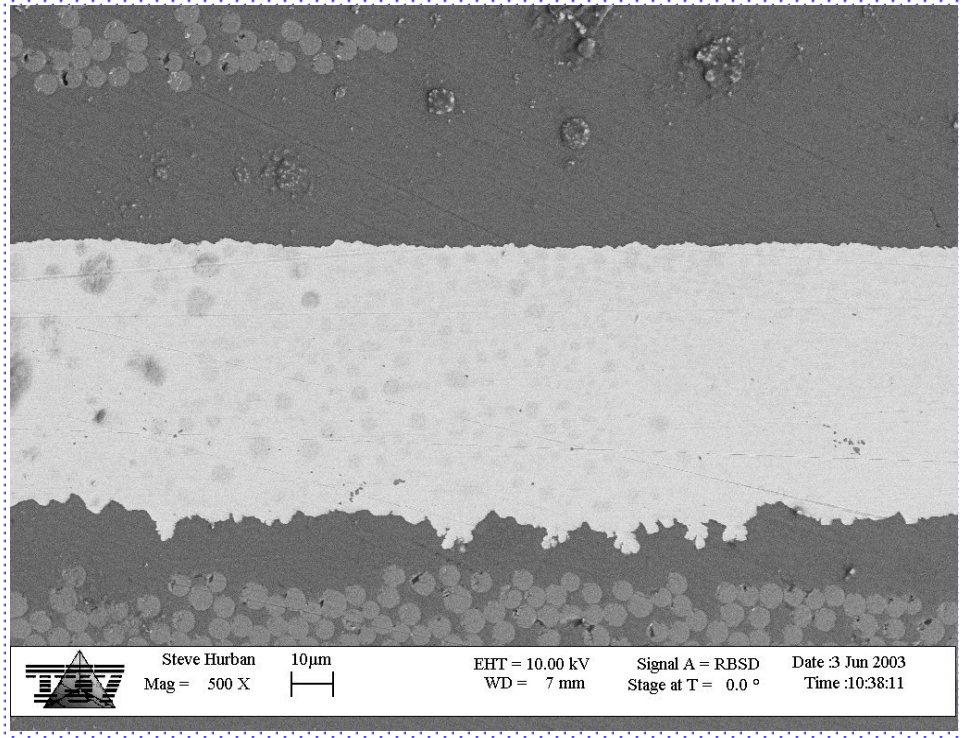
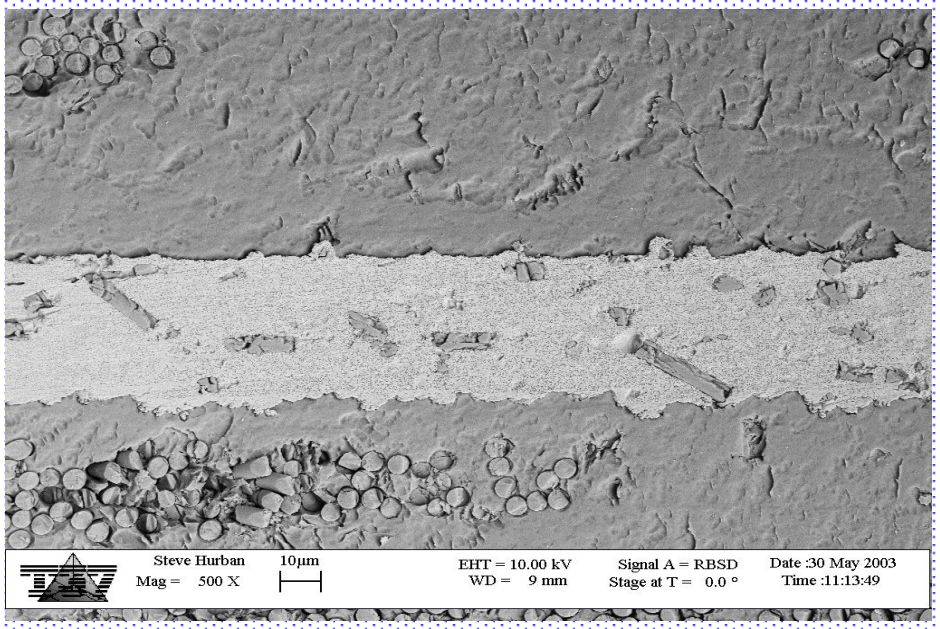
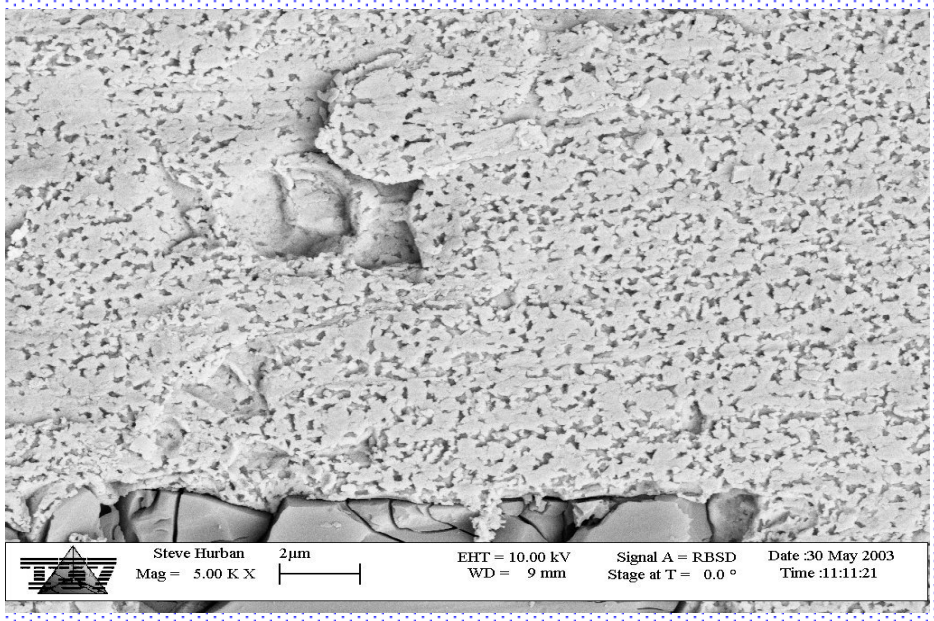
- **Role of wet process in PTH reliability:**
  - Smear removal
  - Cleaner/Conditioner
  - Microetch
  - Seed desposition
  - Electroless Copper

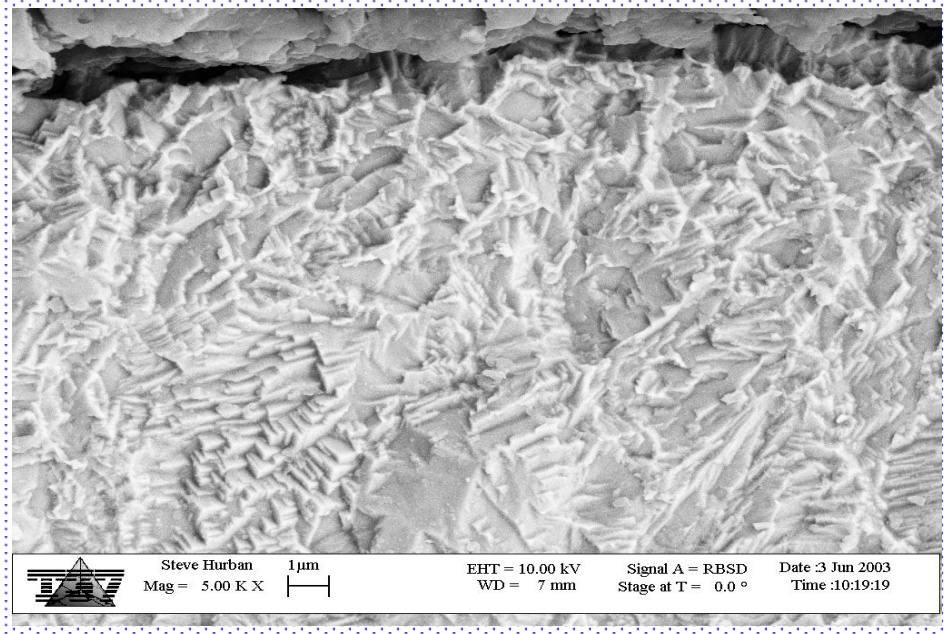




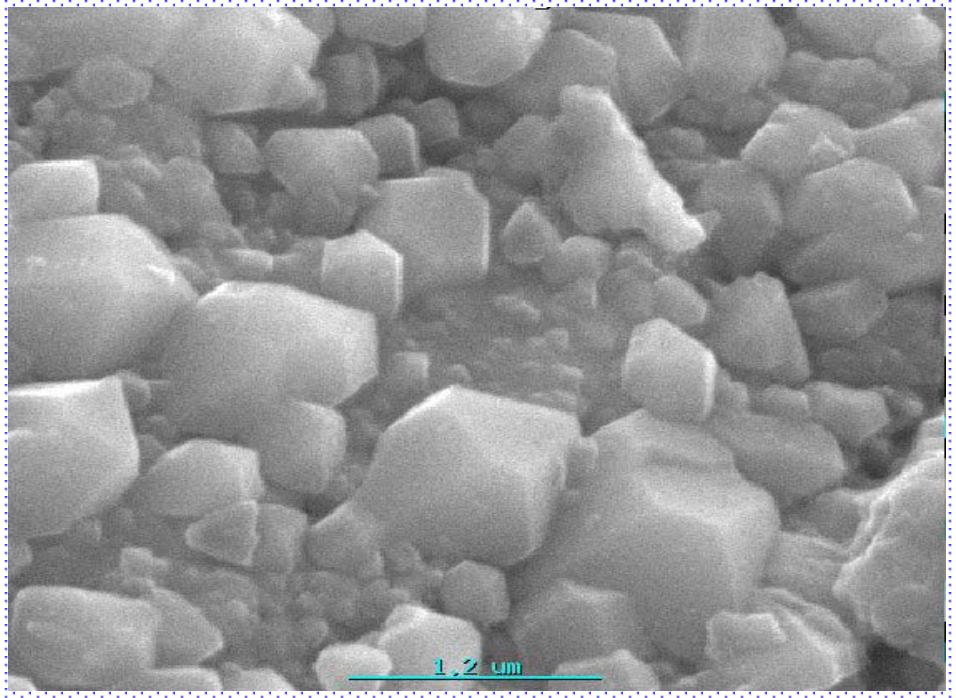
Differences in smear levels

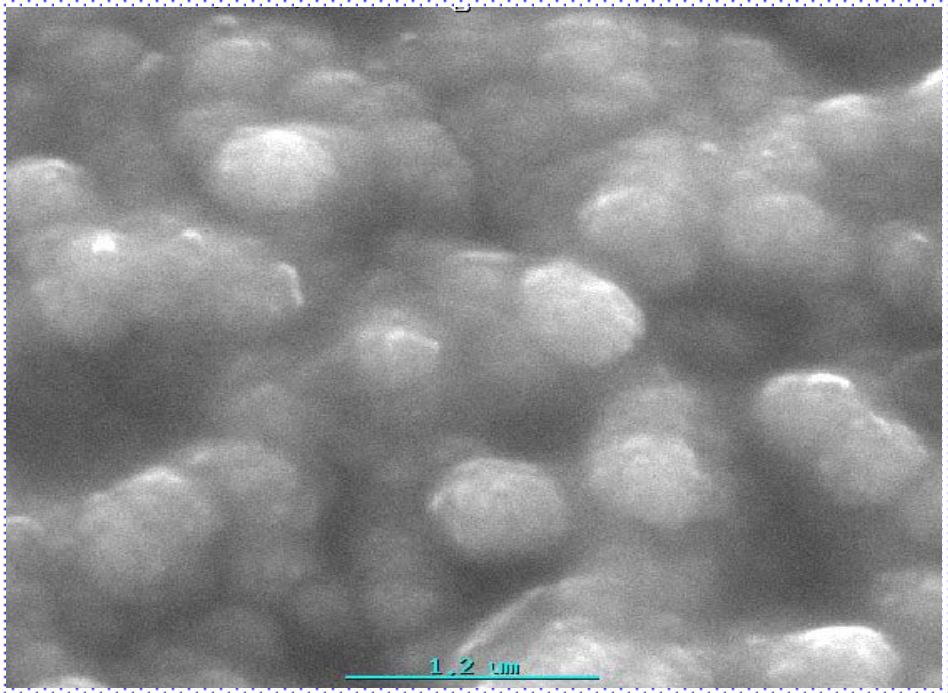






Differences in innerlayer surface topography





Differences in Electroless copper deposit

- **Objectives:**
  - Optimum innerlayer texturing
  - Cleanest surface possible into microetch
  - No foreign species inhibiting etch
  - Is there a way to quantify this?

- **Corrosivity:**
  - Provide a surface prior to microetch that corrodes well
  - Copper that corrodes uniformly
  - Quantify corrosivity of each process step
  - Does it relate to copper grain appearance

- **Methodology:**
  - Electrochemical corrosion testing of each process step
  - Include controls such as incoming and OSP'd copper foil
  - Tafel plots of copper surfaces
  - Record polarization curves
  - Calculate corrosion rates

- **Experimental:**
  - Process copper clad laminates thru wet process
  - Individual samples removed incrementally as they run
  - Sample 1 thru process step 1
  - Sample 2 thru process steps 1&2, etc

STEP	DESCRIPTION	DWELL & TEMPERATURE
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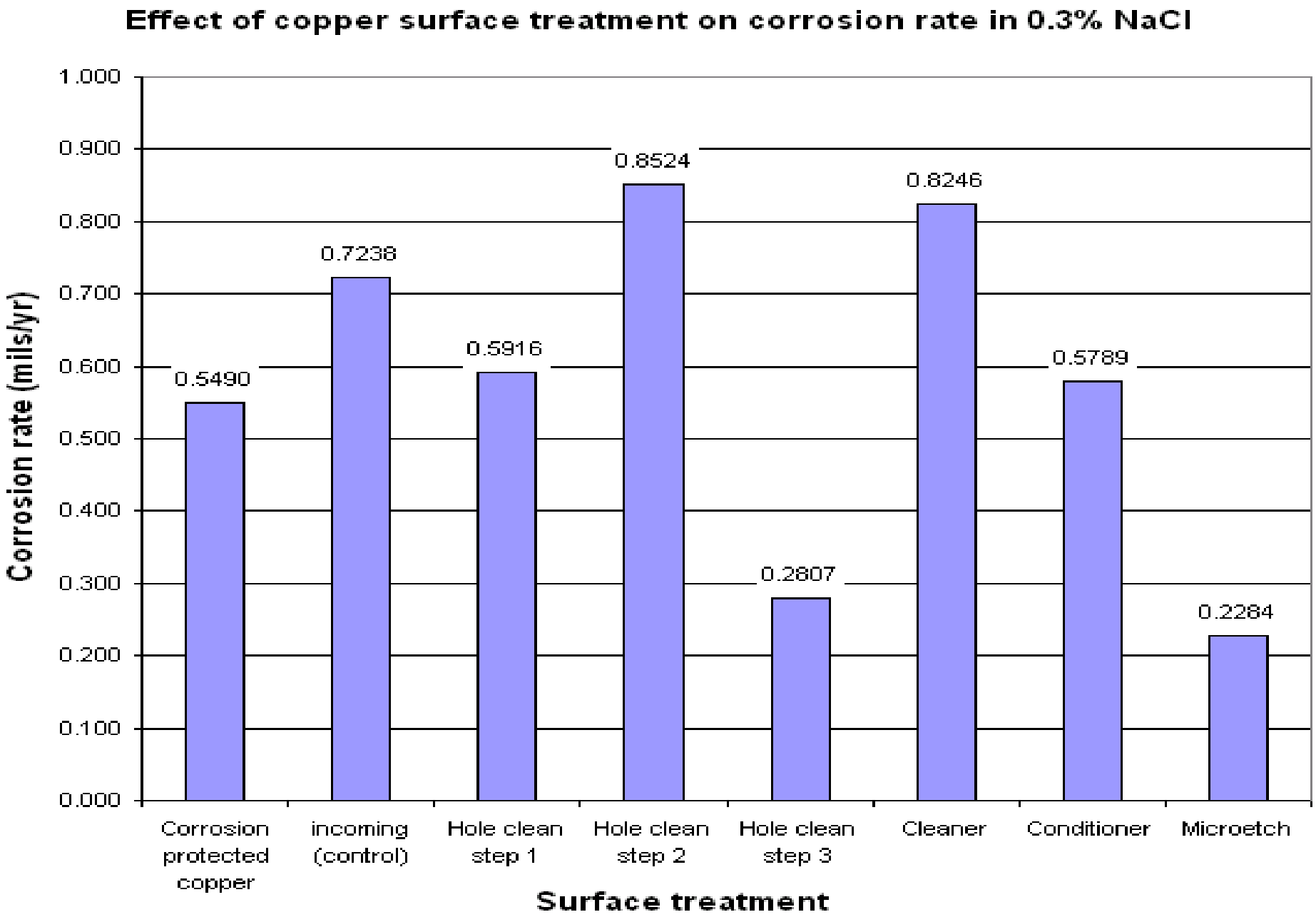
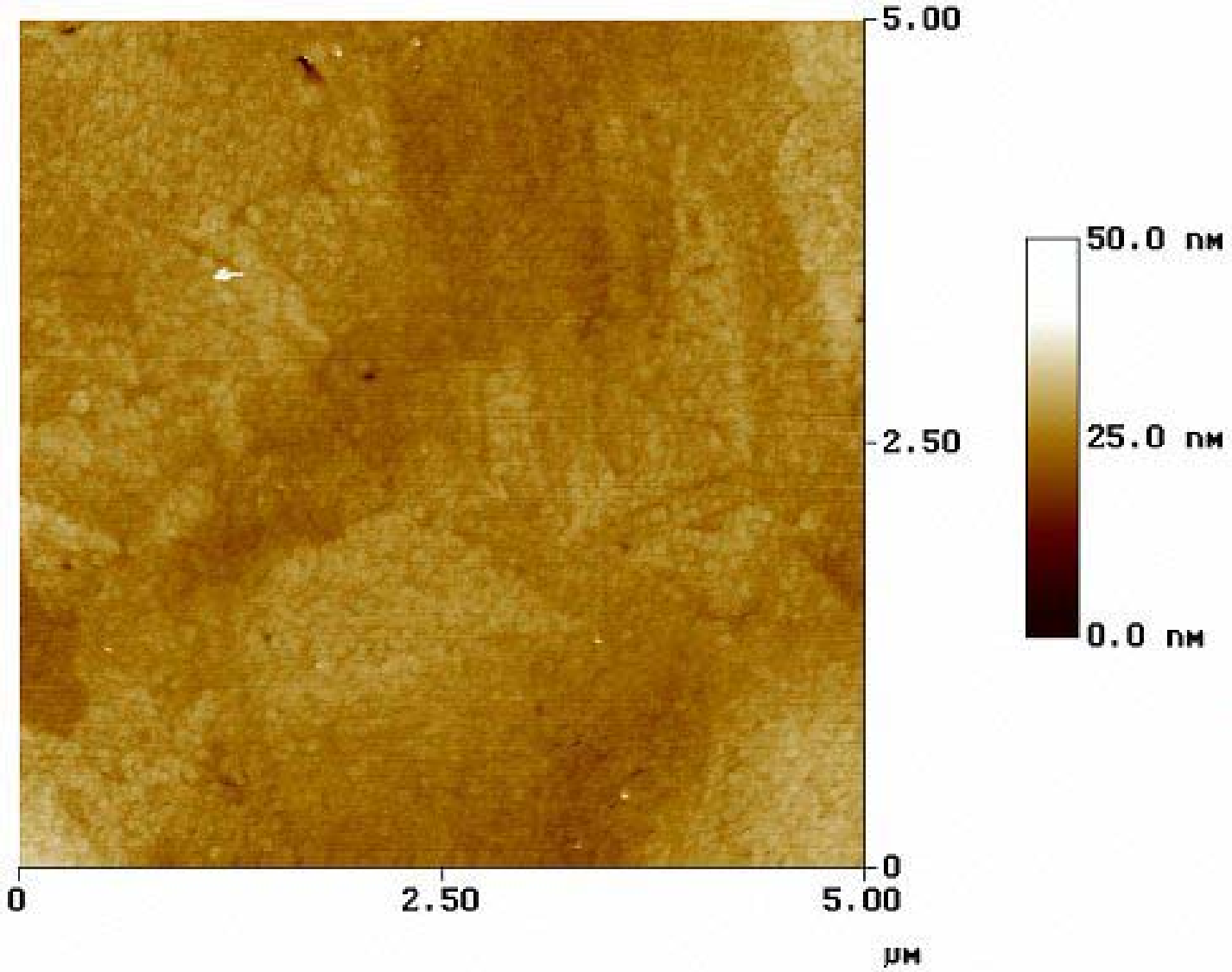
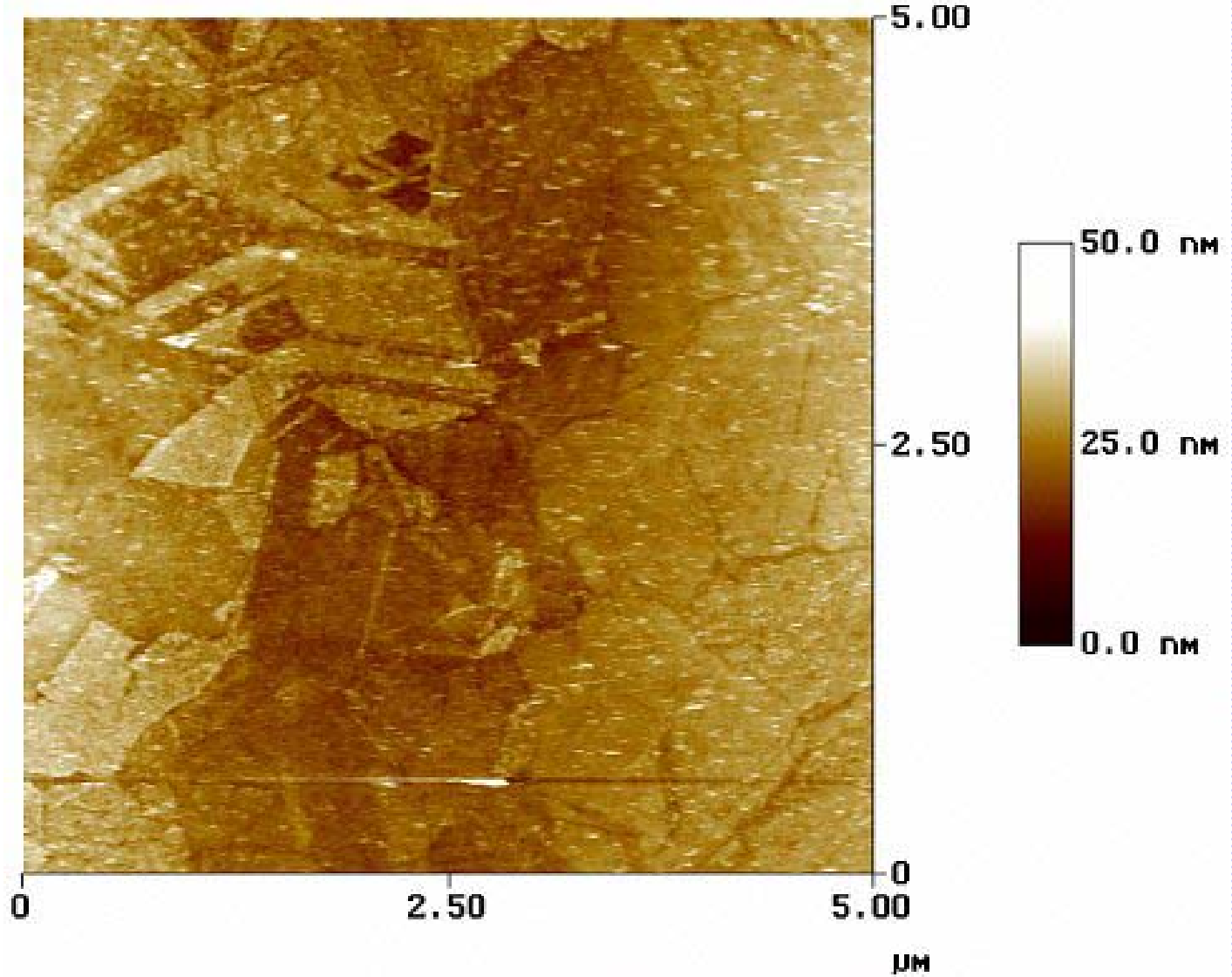
Permanganate	60 g/l permanganate	4 minutes at 75C
Neutralizer	10% v/v hydroxylamine soln.	1 minute at 40C
Cleaner	40 ml/l ethanolamine soln.	1 minute at 50C
Conditioner	100 ml/l conditioner soln.	1 minute at 30C
Microetch	120 g/l peroxymonosulfate	1 minute at 35C


Effect of copper surface treatment on corrosion rate in 0.3% NaCl
Corrosion rate (mils/yr)
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0.5490
0.7238
0.5916
0.8524
0.2807
0.8246
0.5789
0.2284
Corrosion protected copper
incoming (control)
Hole clean step 1
Hole clean step 2
Hole clean step 3
Cleaner
Conditioner
Microetch
Surface treatment

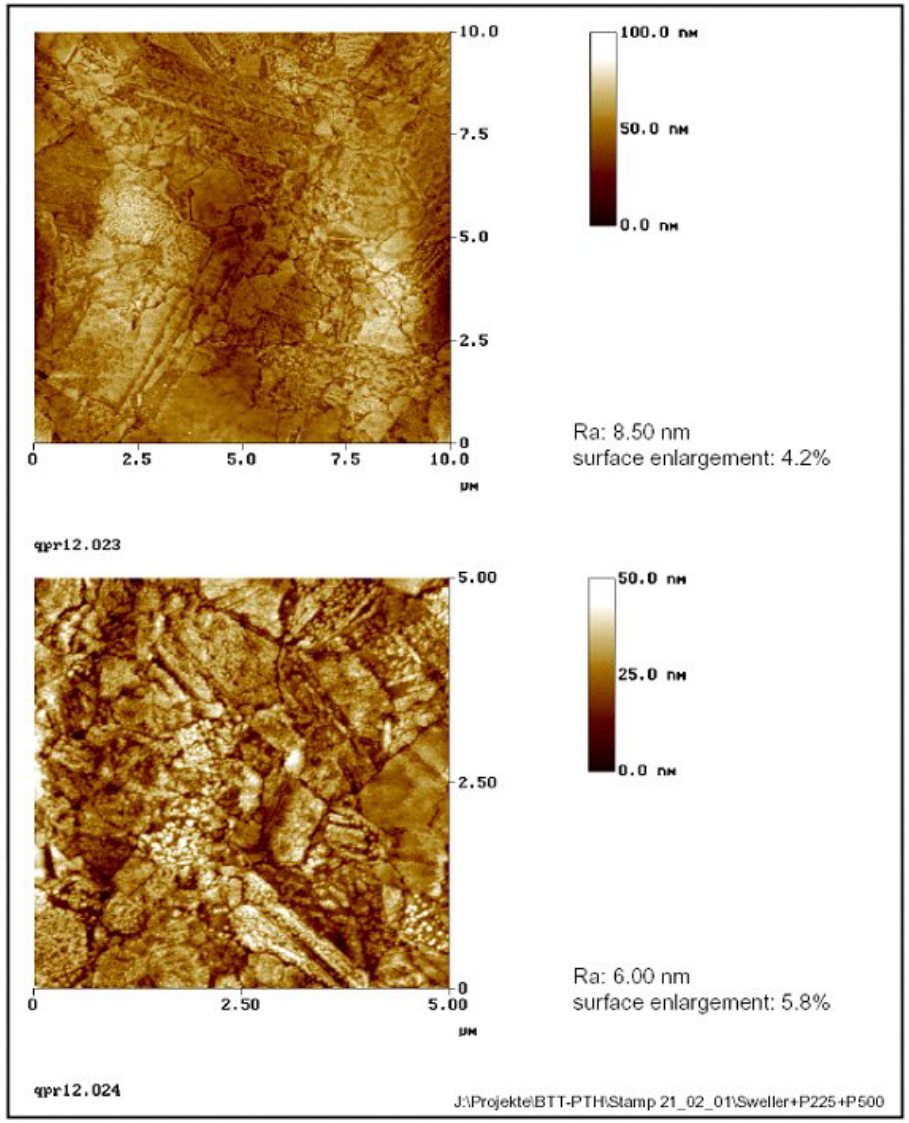
- **Quantitative observations:**
  - Significant drop in corrosivity after Neutralizer step
  - Organic trace on surface could inhibit corrosion
  - 'Cleaner' step removes trace and increases corrosivity
  - Trace-free innerlayer into Seed/Eless



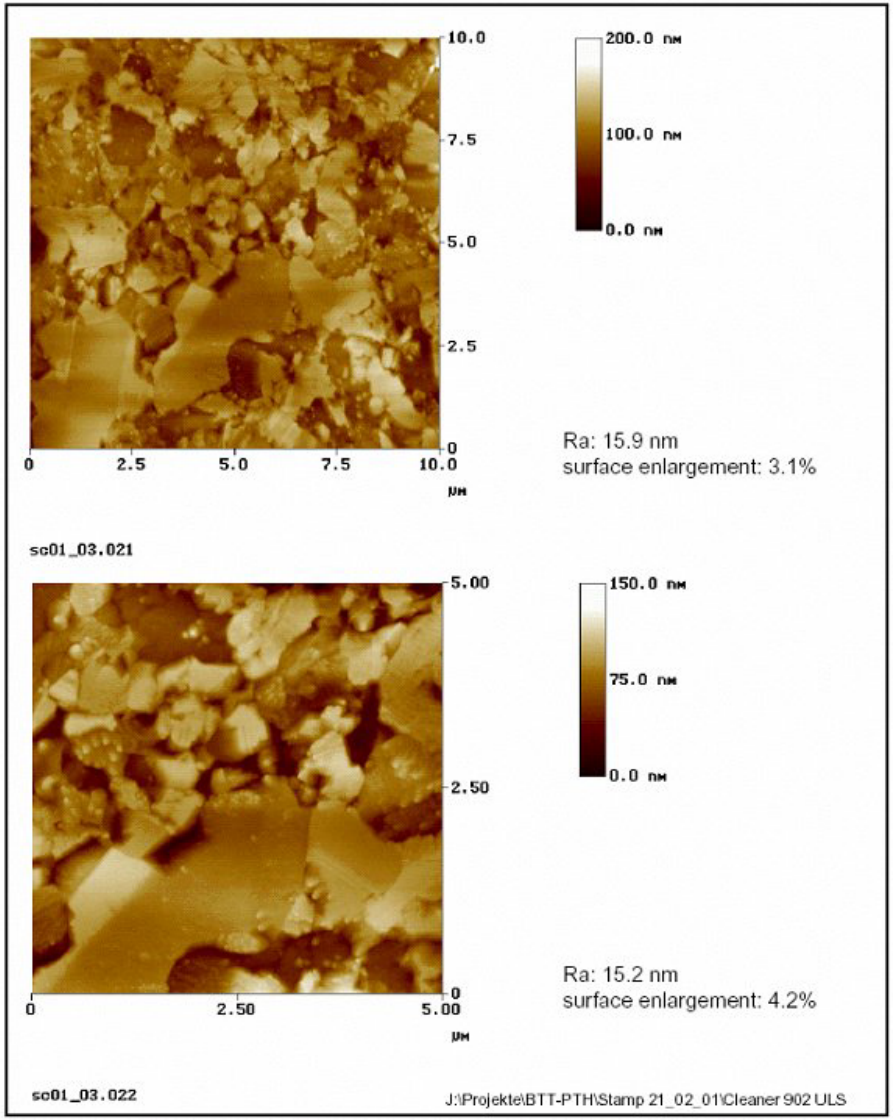
AFM image observed from copper surface incoming to the wet process



AFM image observed from copper surface after sweller and permanganate



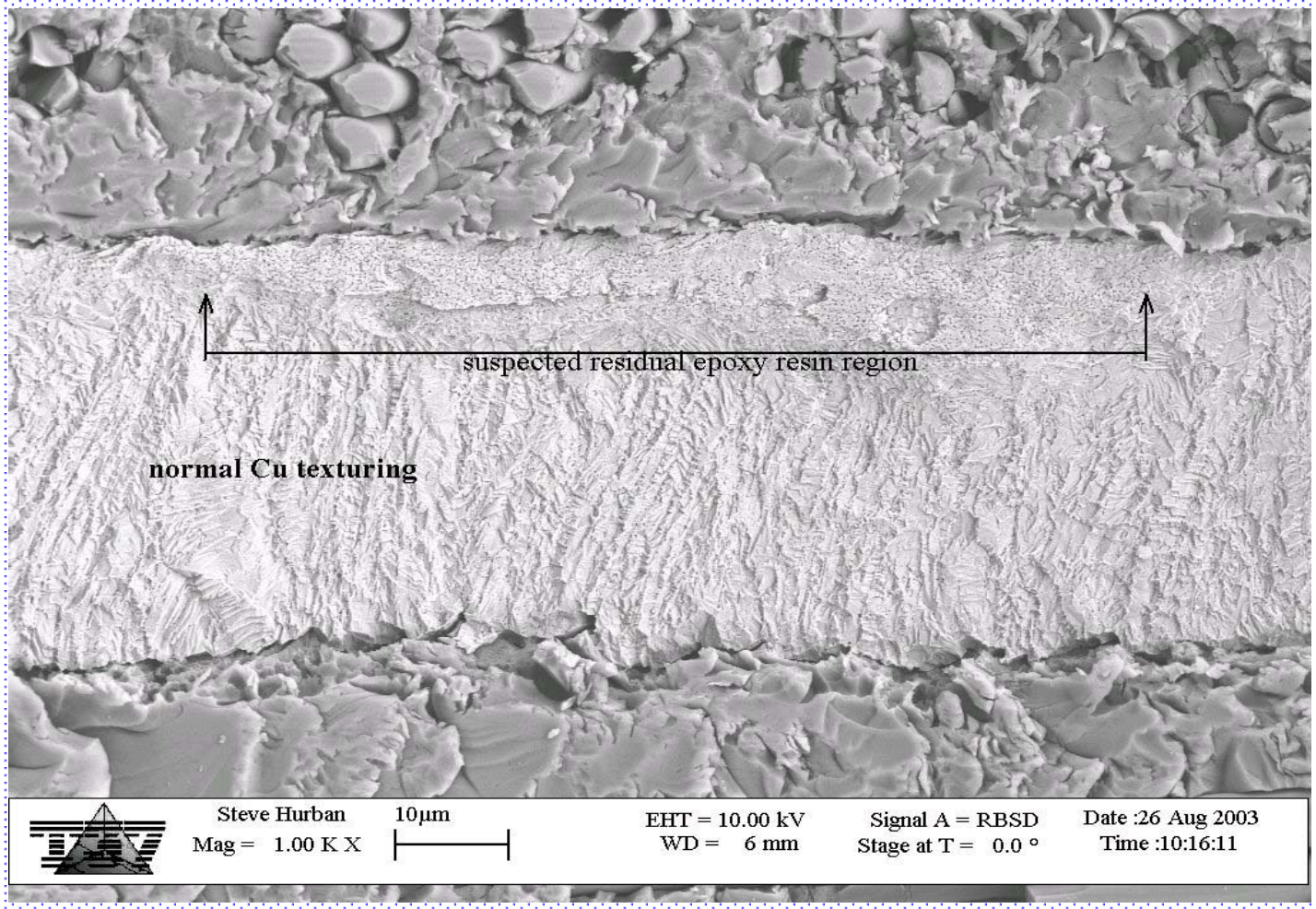
AFM image observed from copper surface treated in sweller, permanganate, neutralizer



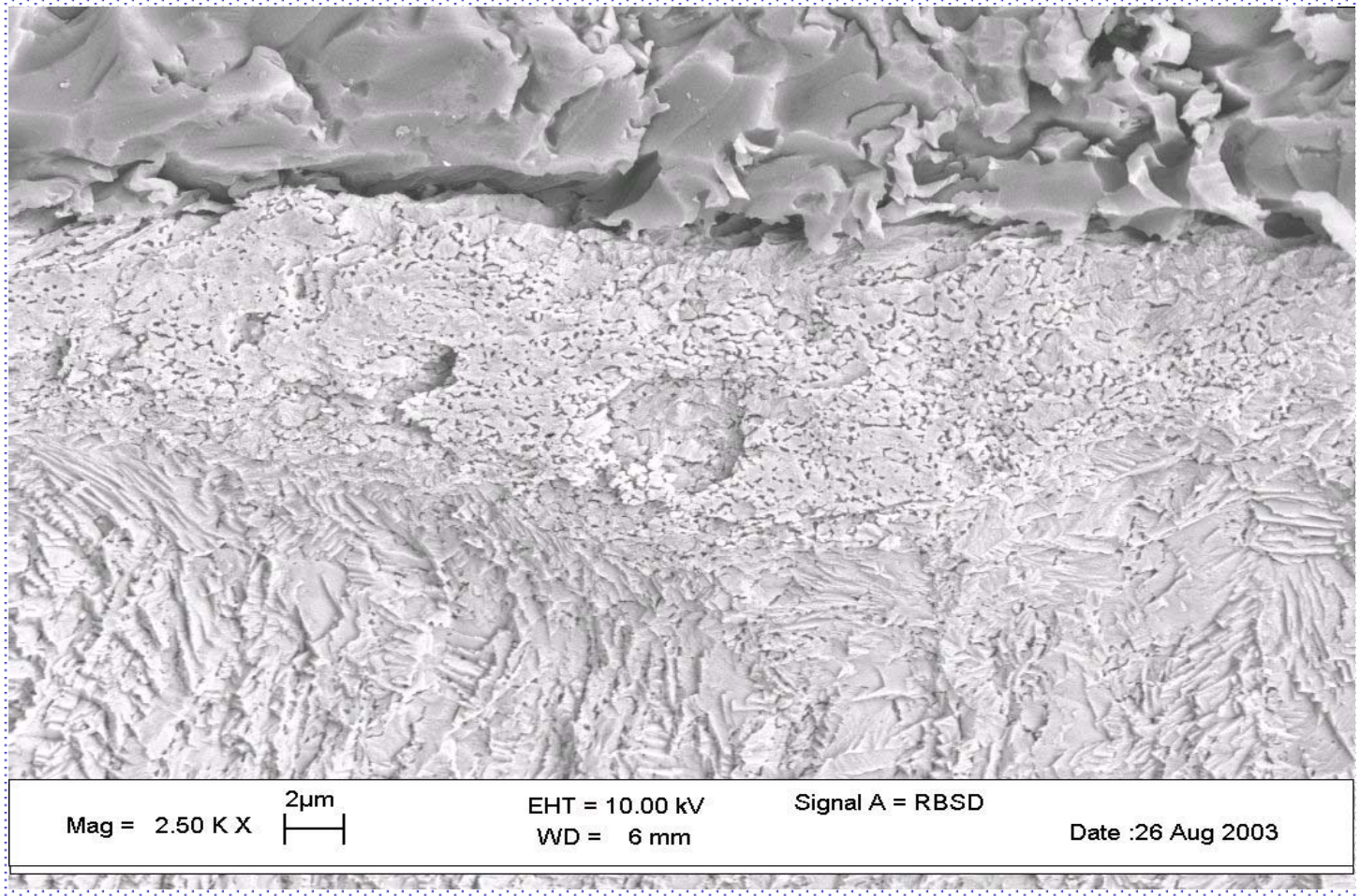
AFM image observed from copper surface treated thru desmear & cleaner

- **Qualitative observations:**
  - Distinct surface appearances by wet process steps
  - Surface after 'Cleaner' step shows clear grain with no traces
  - Provides a surface to microetch that leads to uniform texturing

- **Impact of organic traces on reliability:**
  - Lack of uniform texturing thru microetch
  - Electroless copper adhesion to innerlayer
  - Innerlayer Separation post solder shock



- **Lack of texturing possibly due to organic trace on innerlayer**



- Lack of texturing possibly due to organic trace on innerlayer (higher mag)

- **Conclusions:**
  - Process steps can influence copper surface properties
  - Control of these steps provides increased reliability leverage
  - Corrosion rates appear to match well with surface appearance using AFM microscopy