SETNA

IEEE ESTC CPMT GRENOBLE 2016

SESSION 14
MATERIALS AND PROCESSES
FOR ADVANCED PACKAGING

UTILIZATION OF ATMOSPHERIC PLASMA SURFACE PREPARATION TO IMPROVE COPPER PLATING PROCESSES.

Eric Schulte[1], Gilbert Lecarpentier[2]

SETNA Corporation LLC

[1] ESchulte@set-na.com

[2] GLecarpentier@set-na.com

INTRODUCTION: PRE-PLATING SURFACE PREPARATION

- Many steps in semiconductor processing and packaging benefit from pristine surface preparation, such as descuming of photoresist, removal of native oxides, and surface activation.
  One particularly important surface process is the **preparation prior to copper plating**.

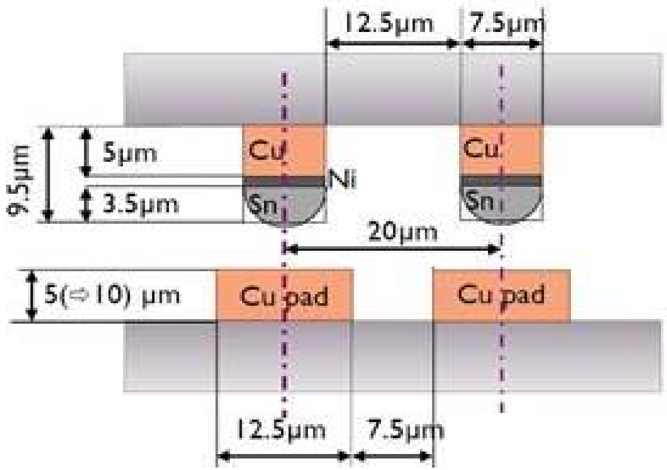
- There are 5 performance aspects to preparing surfaces for plating with Atmospheric Plasma:

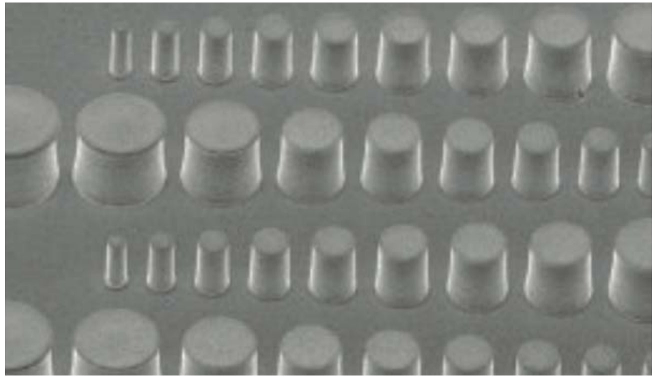
1. Descum of photoresist residue,
2. Removal of oxidation from plating base,
3. Activation of photoresist for wetting down into small photoresist apertures,
4. Optional passivation of de-oxidized plating base by including N_2 in the downstream active chemistry,
5. Optional preservation of surface activation by introducing water molecules (H_2O) after treatment.

The first four of these aspects can be accomplished simultaneously with a single process and apparatus.

INTRODUCTION: COPPER PILLAR INTERCONNECTS

- The transition to copper as a conductor is one of the most significant changes in semiconductor manufacturing history. Technologies such as Copper Pillar and TSV plating are used for micrometer scale interconnects.

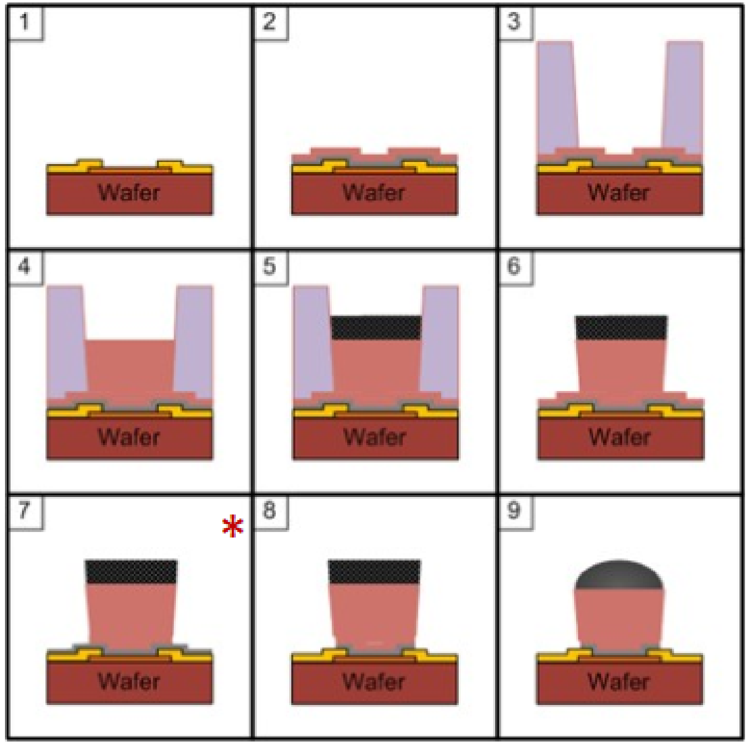



Electroplated copper pillars after photoresist strip

- Photoresist masking is necessary for plating small features such as copper pillar interconnect technology where the pillars are on the order of 5 to 15 µm in diameter.
- The aspect ratio of copper pillars is often high (bumps can be taller than their diameter), leading to more serious wetting issues during plating.

CU PILLAR BUMPING USING ELECTROPLATING

- Cu pillar is plated up from a Cu seed layer. Cu plating uniformity is critical.
- The Cu pillar is typically capped with Sn or SnAg.

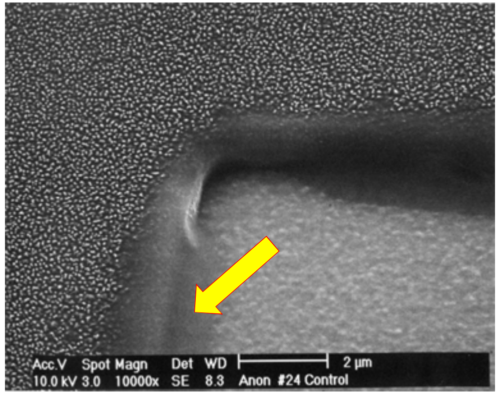
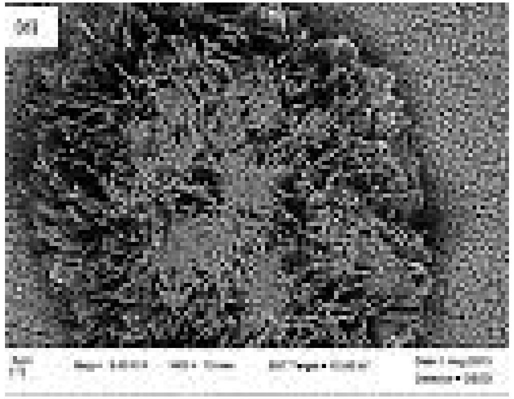
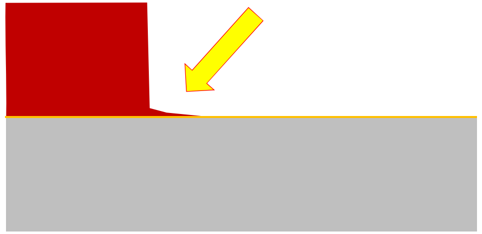
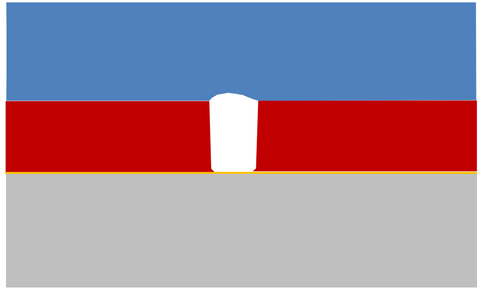


1. Wafer (zoom into pixel pad)
2. Sputtering of adhesion/Barrier & Seed layer for electroplating
3. Photolithography
4. Plating of under bump metal (Cu)
5. Plating of Tin
6. Photoresist removal
7. Etching of seed layer (wet & dry)
8. Etching of adhesion/barrier layer
9. Solder reflow

EMERGING FINE-PITCH BUMP BONDING TECHNIQUES SAMI VAEHAENEN – CERN PH-ESE LCD-WG4 Vertex detector technology meeting 3-September-2010.

CHALLENGES WITH COPPER PLATING

The following **surface conditions** strongly affect yield and throughput:

Photoresist Residue	Seed Layer Oxidation	Wetting into PR Features
		
		
Dimension Control	**Non-Uniform Nucleation**	**Bubble Skip**

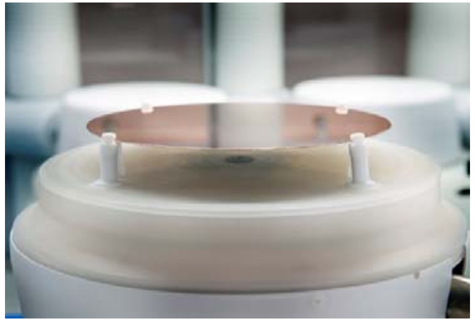
HOW DO WE DEAL WITH THESE ISSUES?

Oxygen Asher
Descumming

+

Oxide Etch
Oxide Removal

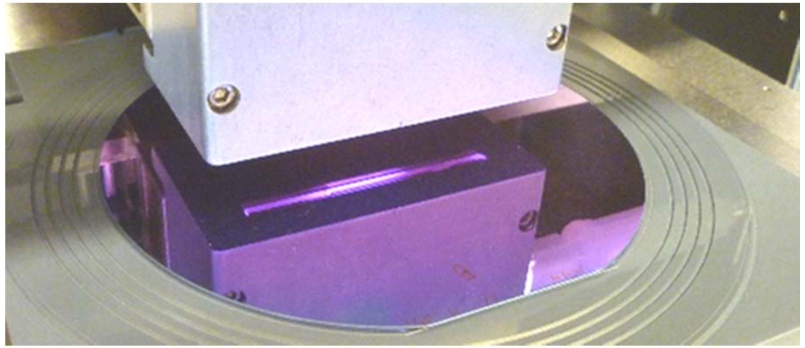
+



Pre-Wetting Station
Surface Activation

OR

Atmospheric Plasma
(Ontos)



$He+H_2+N_2$
Reducing Chemistry

<u>Simultaneous</u> Descum, De-oxidation, Surface Activation

OXYGEN ASHING VS. ATMOSPHERIC PLASMA

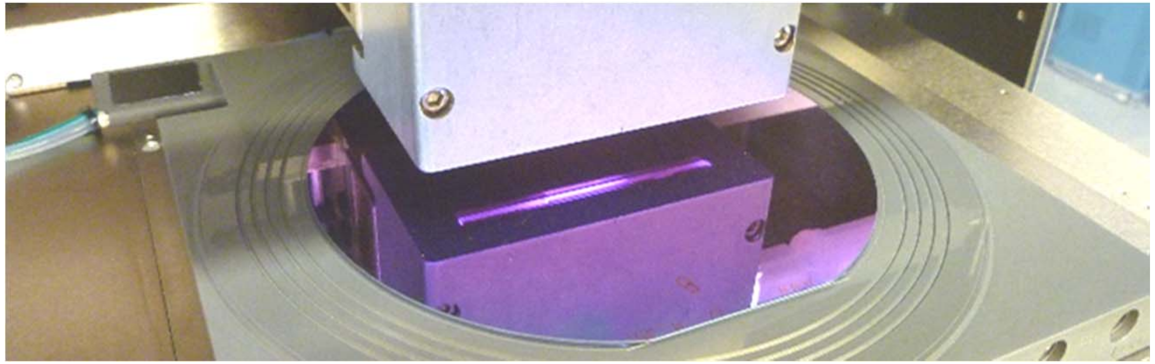
- Oxygen ashing traditionally used to descum photoresist residues has several disadvantages:
  - ☹ It grows additional oxide on the thin layer of copper plating base.
  - ☹ It changes linewidths in the photoresist pattern.
  - ☹ It leaves the photoresist surface hydrophobic, and
  - ☹ It requires the use of a vacuum system.

- Atmospheric Plasma with reducing gas chemistry provides simultaneous:
  - ☺ **Descuming** of photoresist residue
  - ☺ **Removal of oxidation** from plating base.
  - ☺ Hydrophilic **activation of photoresist** for instantaneous wetting down into small photoresist apertures.
  - ☺ **Optional passivation of de-oxidized plating base** against re-oxidation.

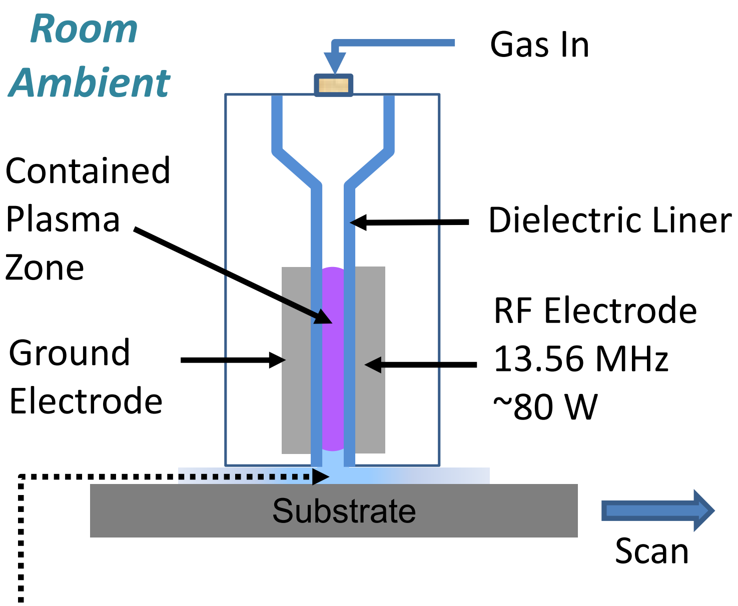
All of this is accomplished in room-ambient conditions, eliminating the need for a vacuum system.
The need for pre-wetting of the wafers, prior to plating, is also eliminated.

WHAT IS ONTOS ATMOSPHERIC PLASMA ?

- Highly-energetic species of the plasma (ions, hot electrons), confined within the plasma head, have such short lifetimes at atmospheric pressure that they are re-combined within a few microns of exiting the plasma zone.
- Chemical radicals with longer lifetimes are still active when contacting the substrate below. These chemical radicals may include atoms of hydrogen, oxygen, nitrogen, or others.



Cross Section of the Plasma-Head

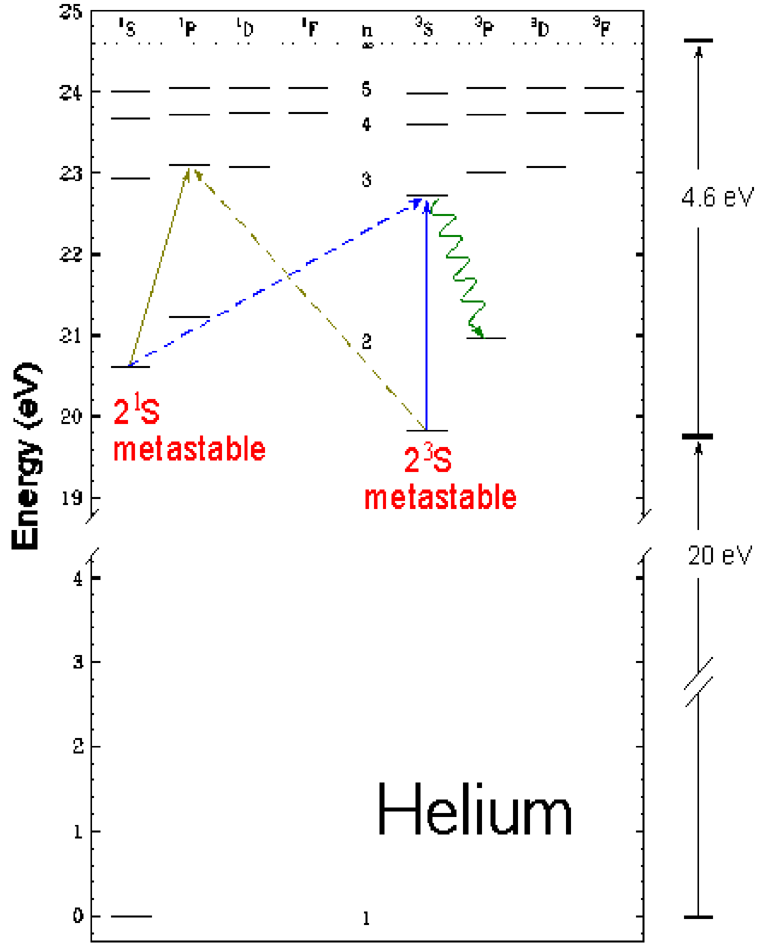


Downstream active radicals

- cool gas (<100°C)
- no ions, no hot electrons.
- Laminar flow excludes atmosphere from process zone

QUANTUM ENERGETICS ACTIVATE SURFACE REACTIONS

- Helium, the atmospheric plasma carrier gas, has two **metastable** energy levels (2^1S and 2^3S) at **19.8 and 20.6 eV**.
- Once an electron is excited into this state by the RF, it can only decay back to ground state by physical **collision** with other atoms.
- This occasionally occurs in the gas phase, but occurs strongly as the metastable Helium atoms **contact the substrate surface**.
- This contact transfers quantum energy directly to the surface atoms and provides **extra activation energy** for surface chemical reactions.



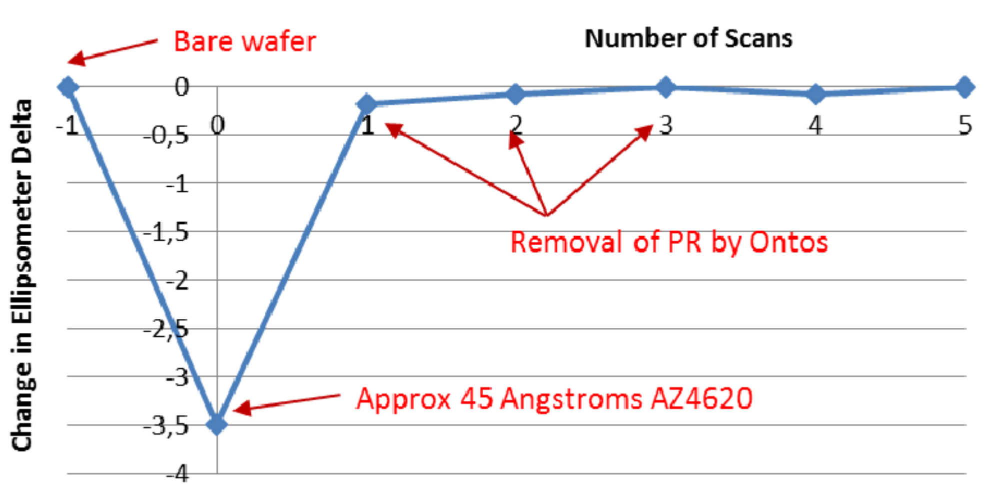
[Energy transfer from He 2^1S and 2^3S are the principal source of excitation for the HeNe laser]

DESCUM OF PHOTORESIST RESIDUE

- In semiconductor processing there exists a slight residue of photoresist material ("scum") in the bottom of a developed-out resist pattern.
- Oxygen ashing in a vacuum system is most often used to remove this scum.

- Ontos takes a different direction by using reducing chemistry (Hydrogen-based excited species) to remove post-develop photoresist scum, while having the advantage that **any existing oxide on the surface of the exposed plating base is reduced** instead of growing more oxide, as occurs with Oxygen-based de-scumming processes.

AZ4620 residue response to Ontos He/H_2/N_2

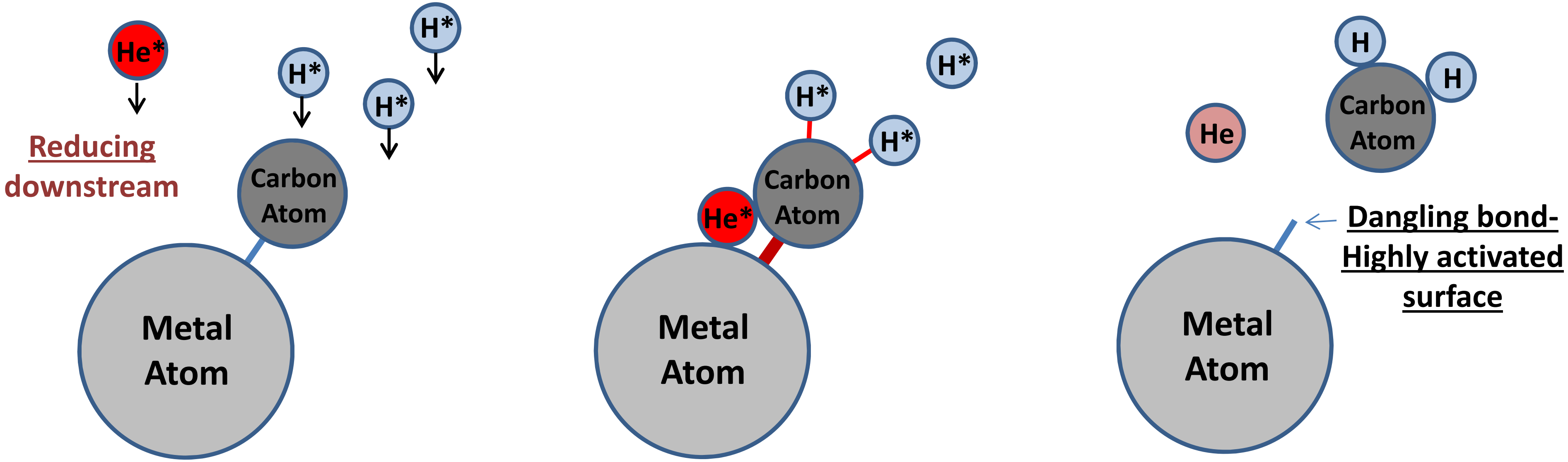


SiO2-coated silicon wafer was over coated with a very dilute solution of positive photoresist (AZ4620) in acetone, and then dried on a hotplate.

DESCUM OF PHOTORESIST RESIDUE

- The flow of downstream gas from the atmospheric plasma head sweeps all room air from the reaction region at the substrate surface.

  This serves a similar purpose as a vacuum system without the need for vacuum chamber, pumping equipment and long pump down times.



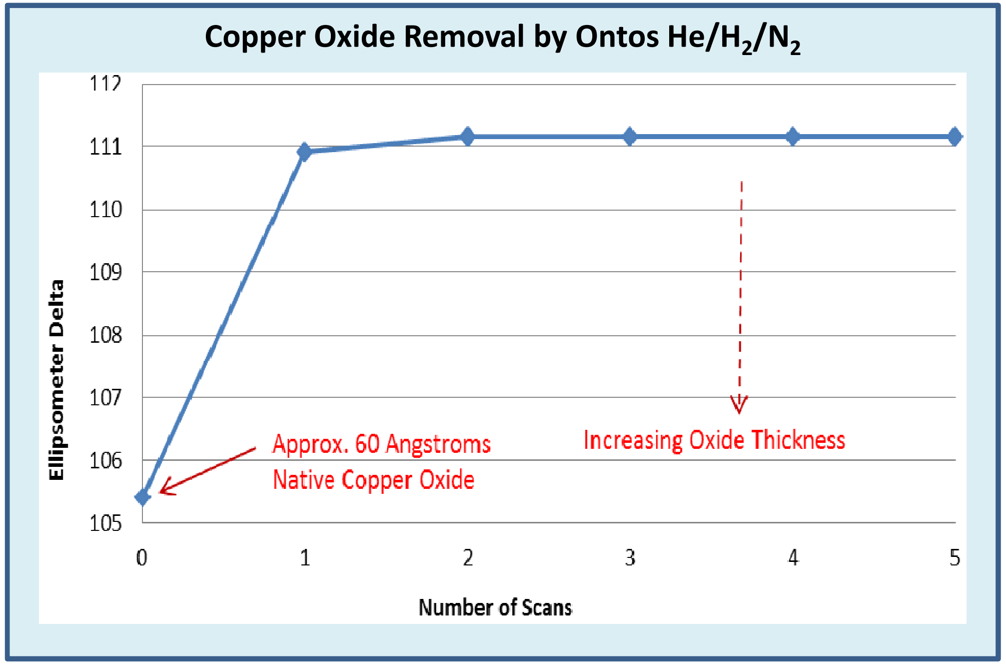
- Reducing reactions are used to remove carbon, Hydroxyl (OH), and other contaminants from the substrate surface.

OXYGEN REMOVAL FROM COPPER SEED LAYER

- Exposed to atmosphere, Copper growths at room temperature a layer of Cupric Oxide (CuO) on the surface. This oxide inhibits the passage of electrical current through the plating base to the plating solution. It results in variable nucleation of plating onto the plating base, and undesirable non-uniformities in plating thickness.
- Traditional photoresist de-scumming with oxygen increases the thickness of this oxidation layer.

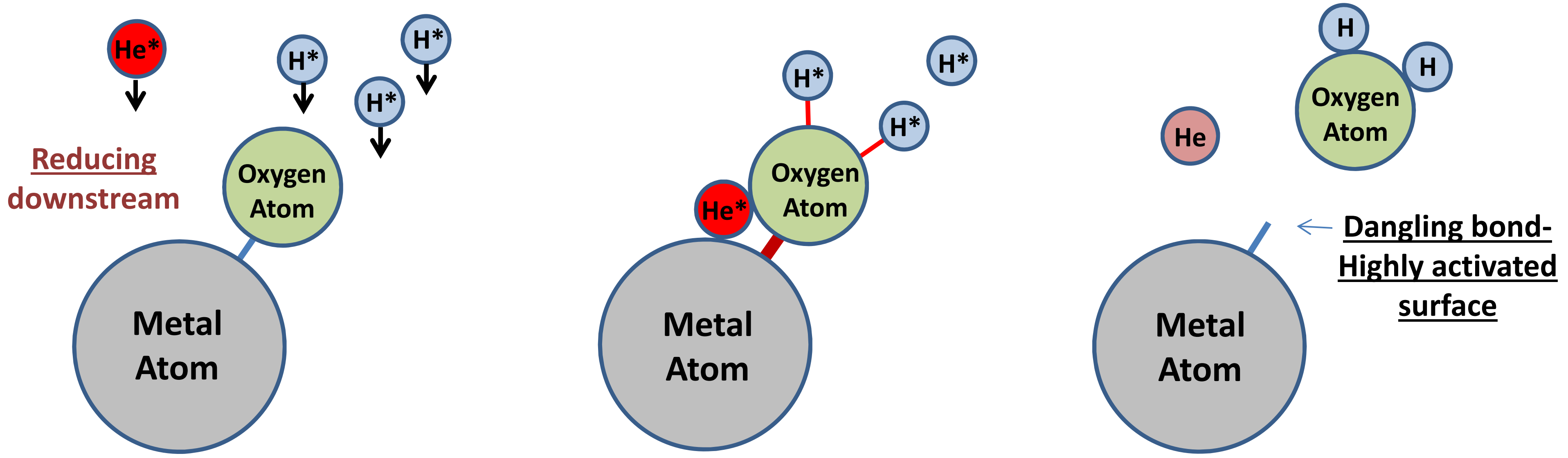
- Ontos Atmospheric Plasma with reducing chemistry (Hydrogen-based excited species) is used to remove oxidation from the plating base.

  A plating base of Nickel responds in a very similar manner.



OXYGEN REMOVAL FROM COPPER SEED LAYER

- Hydrogen radicals (H*) are highly reactive species ready to react with the substrate surface.
- Additionally, the downstream gas flow contains metastable helium atoms which provide approximately quantum energy directly to the substrate surface. This energy helps to activate chemical reactions.

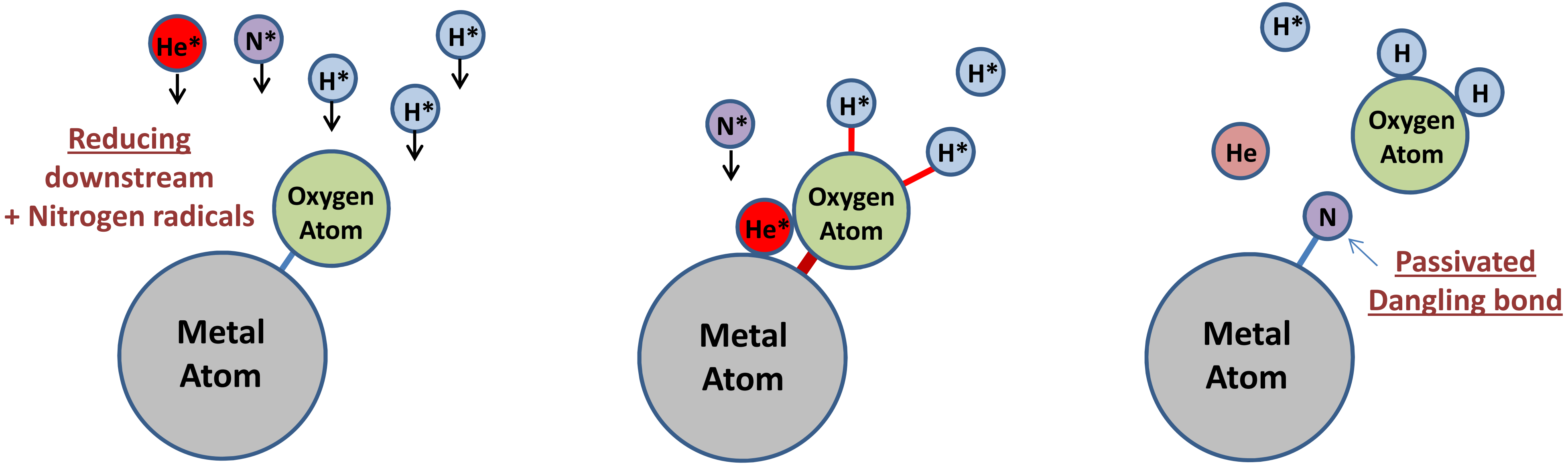


- For example, two H* atoms reacting with an oxygen atom attached to the surface (i.e. a metal oxide) to remove the oxygen from the metal atom.

Oxide can be reduced from In, Sn, Ni, Cu, Sb, Ag, Au, and more.

PASSIVATION AGAINST COPPER RE-OXIDATION

- Adding Nitrogen to the Atmospheric Plasma supplies Nitrogen Radicals (N*)



- The Nitrogen Atoms occupy the dangling bonds and inhibit re-oxidation.
- The Nitrogen-terminated surface is still a highly polar binding site for water molecules, resulting in extreme wetting of the surface upon contact with the plating bath.

Typical passivation lasts for 20+ hours on Copper.

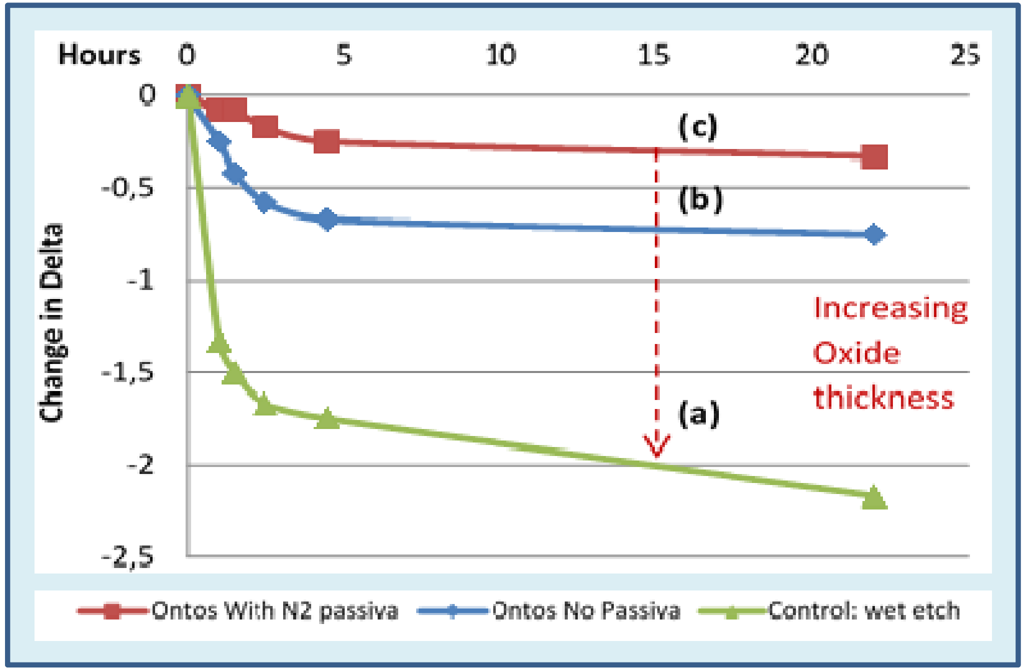
PASSIVATION AGAINST COPPER RE-OXIDATION

- With the addition of Nitrogen Radicals in the downstream from the atmospheric plasma, the de-oxidized Copper plating base can be passivated to inhibit re-oxidation of the Copper with exposure to air.
- Graph shows the re-oxidation of Copper as a function of time for 3 different conditions:

a) Fresh clean copper with no surface treatment

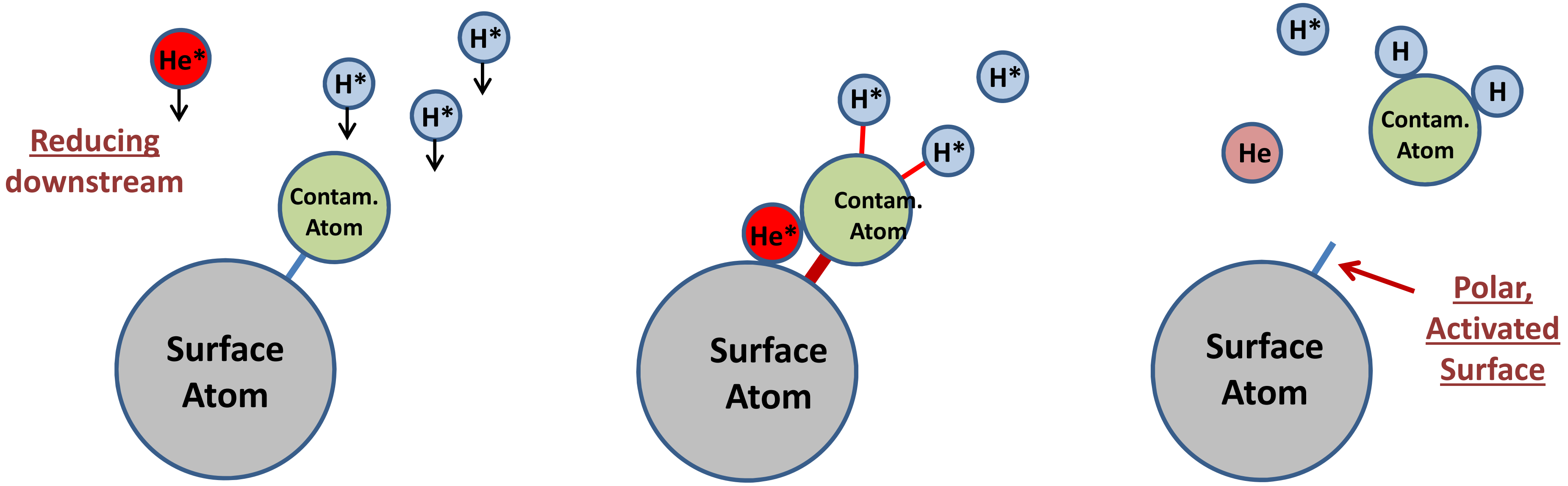
b) Copper treated with He/H_2 only

c) Copper treated with $He/H_2/N_2$



SURFACE ACTIVATION

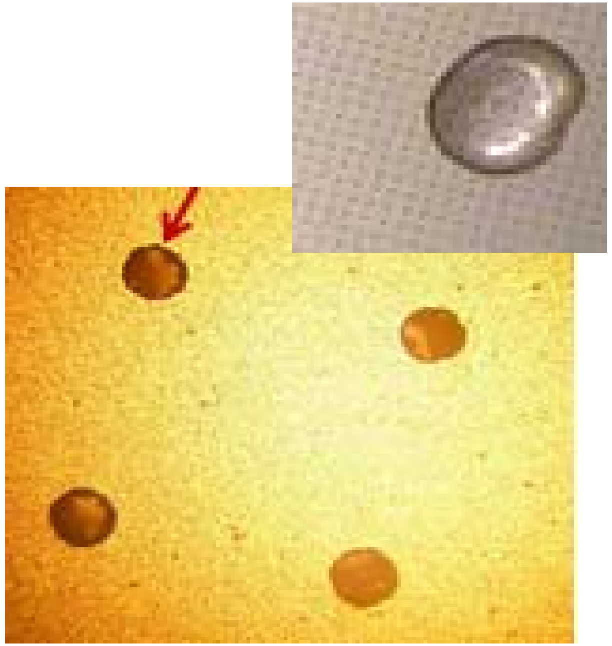
- Downstream reactive radicals and metastable Helium atoms remove surface contaminant atoms leaving behind a dangling bond

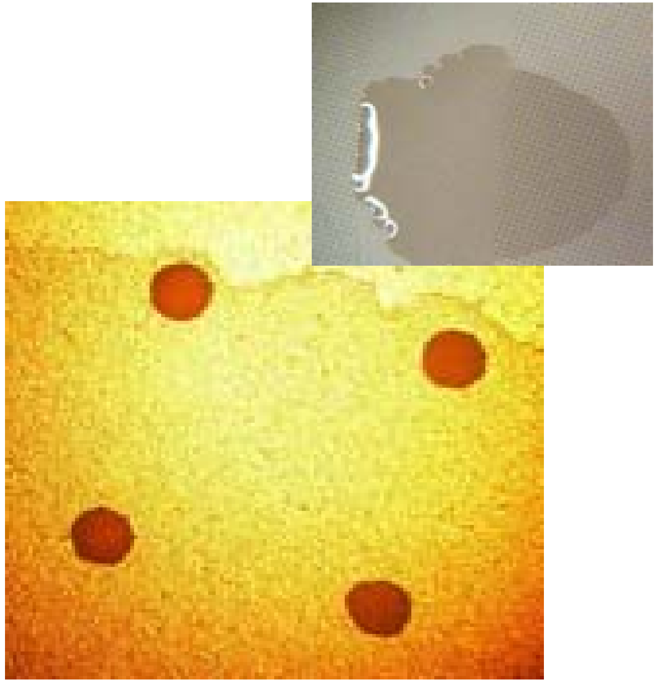


- This dangling bond acts as a highly polar binding site for water molecules, resulting is extreme wetting of the surface upon contact with the plating bath.

Typical activation lasts for many hours on metals; it can last for days on dielectrics, photoresist.

ACTIVATION OF PHOTORESIST FOR WETTING





***Without** Atmospheric Plasma*

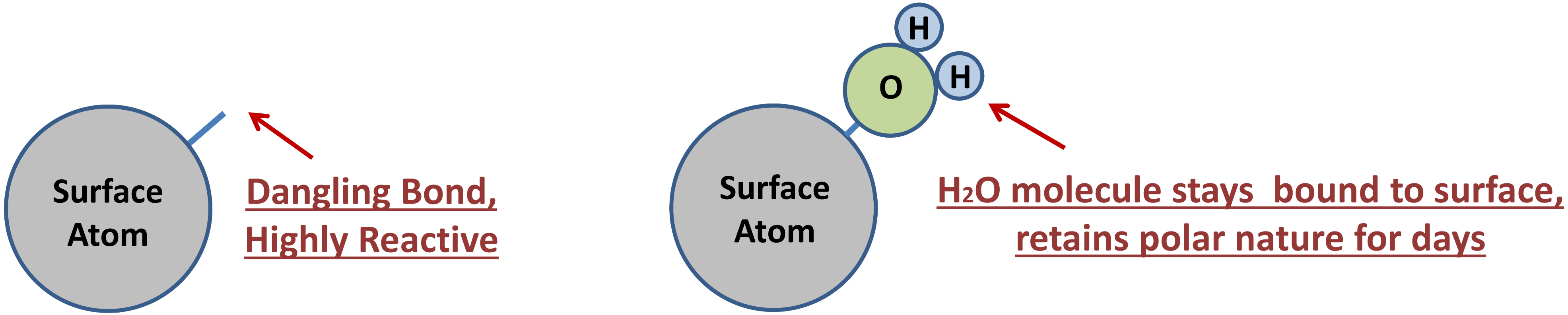
- Entrapped air prevents plating solution from entering small PR features.
- Results in "Skip" plating.

***With** Atmospheric Plasma*

- Surface-activated photoresist draws plating solution into smallest PR features.
- No Skips!

PRESERVATION OF ACTIVATED SURFACE

- Dangling bonds will garner Oxygen, Carbon, Hydroxyl (OH), etc. and lose their polarity.

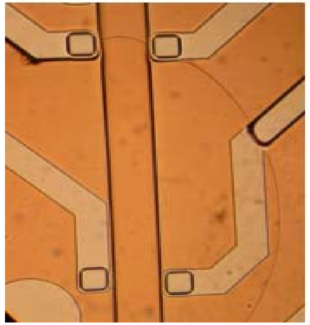


- If the substrate is treated with water after the downstream surface treatment, H_2O molecules will bind to the activated polar surface and remain as a physisorbed polar monolayer on the surface, even after nitrogen blow-off of excess water.
- The physisorbed water molecules are stable in air and remain on the surface for many hours inhibiting the attachment of oxygen or carbon to the substrate surface. Even days later, this layer of water molecules remains attractive to aqueous solutions and enables exceptional wetting on all surfaces.

Typical H_2O preservation lasts for 1-2 days on both Copper and photoresist

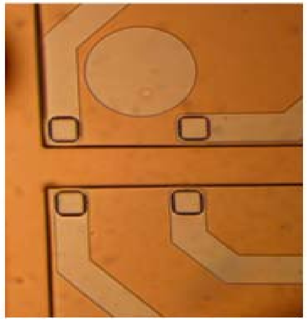
OPTIONAL H_2O PASSIVATION OF ACTIVATED SURFACES

Photoresist and copper plating base wetting capability



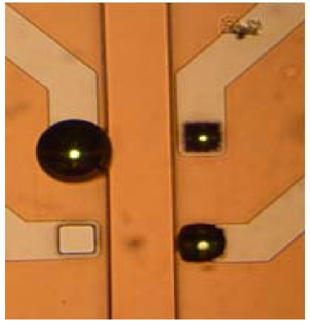
Immediately after downstream treatment as described.

No bubbles are present due to the exceptional wetting properties of the as-treated surfaces.



Same wafer 24 hours later after being re-introduced to an aqueous solution.

No bubbles are present; the wetting properties of the surfaces were preserved by the first water exposure.



The wafer received downstream treatment, but was left in air for 24 hours (no water treatment).

After introduction to aqueous solution, bubbles are seen in the geometries indicating that the surfaces have lost much of their wetting properties.

CONCLUSIONS

- We have demonstrated that Atmospheric Plasma provides a rapid and effective surface treatment which enhances subsequent plating processes. No vacuum system is required, thus enabling continuous throughput.
- With a single surface treatment process, we achieve:
  1) Descum of the photoresist pattern.
  2) Reduction of oxidation on the exposed plating base layer.
  3) Passivation of the plating base to inhibit oxide regrowth
  4) Activation of the photoresist surfaces to provide thorough wetting even in high-aspect-ratio features.
- Additionally, we have shown the use of a water dip to stabilize the activated surfaces for many hours.

SETNA

GRENOBLE 2016

SESSION 14
MATERIALS AND PROCESSES
FOR ADVANCED PACKAGING

THANK YOU FOR YOUR ATTENTION

UTILIZATION OF ATMOSPHERIC PLASMA SURFACE PREPARATION TO IMPROVE COPPER PLATING PROCESSES.

Eric Schulte[1], Gilbert Lecarpentier[2]

SETNA Corporation LLC

[1] ESchulte@set-na.com

[2] GLecarpentier@set-na.com