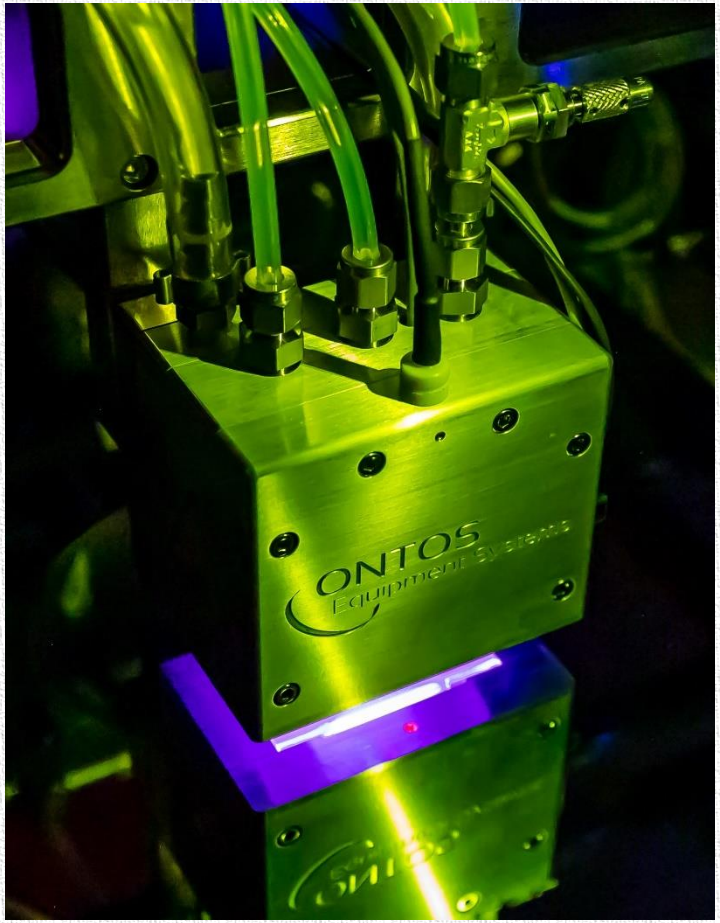
ONTOS
Equipment Systems

Semiconductor Processing with Ontos Atmospheric Plasma

Eric Schulte, September 2021

www.ontosplasma.com

PREAMBLE

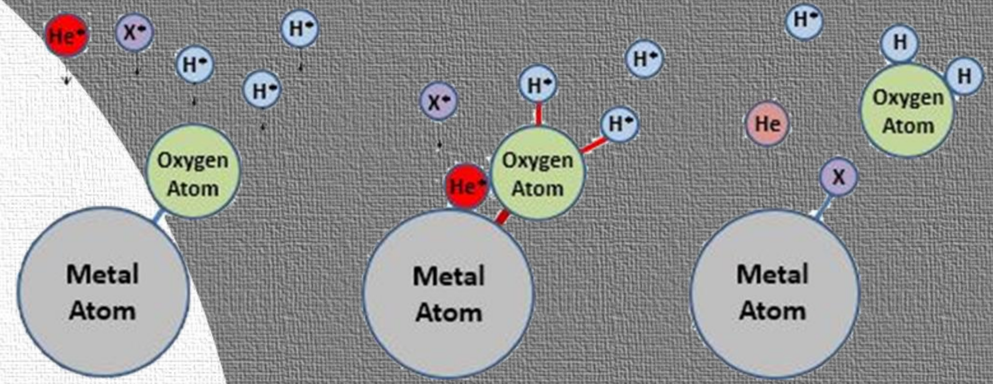


ONTOS is plasma system for Surface Preparation using a **patented** Atmospheric Plasma with a **unique design** enabling using **oxidizing** or **reducing** chemistry, without any modification.

ONTOS performs cleaning, eliminates the organic contamination, removes oxidation and activates surfaces.

An **Innovative Process** applies a gaseous passivation that delay the re-oxidation of the metallic surfaces.

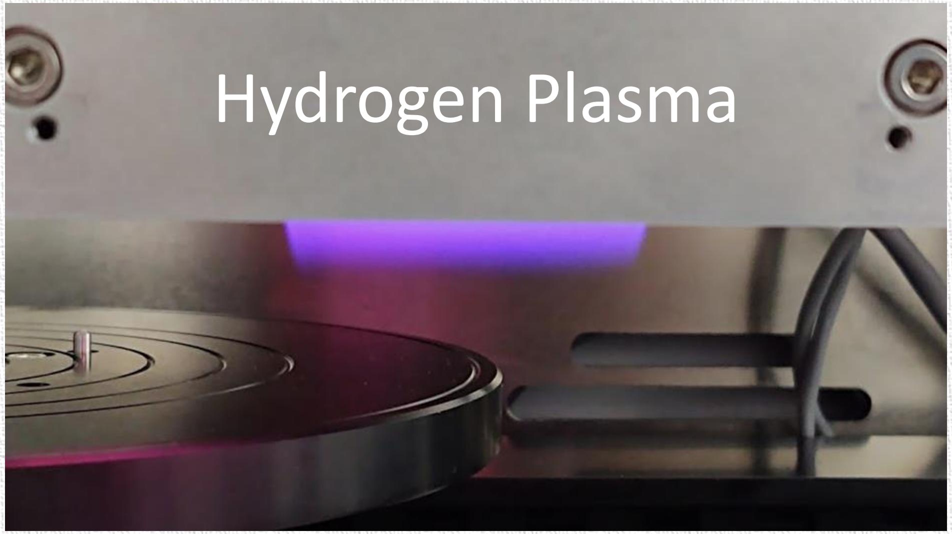
PHYSICAL CHEMISTRY INSIGHTS

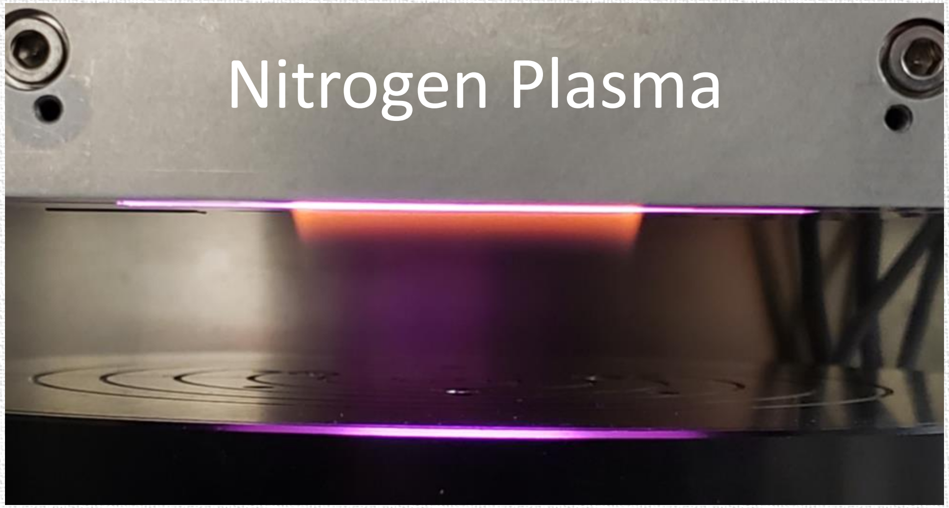


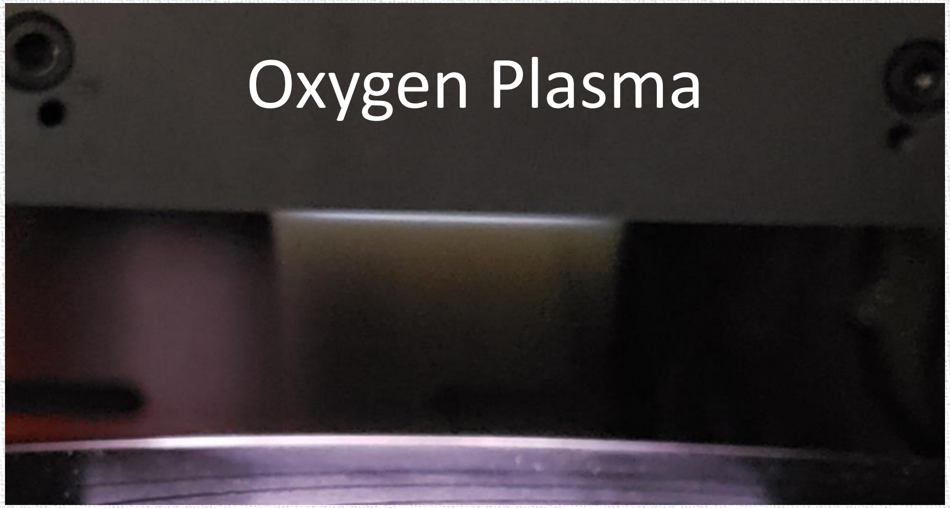
ONTOS Equipment Systems

ONTOS Atmospheric Plasma (Chemistries)

- ONTOS Atmospheric Plasma – Base System Gases:
  - Helium (carrier gas)
  - Helium/Hydrogen (reducing chemistry)
  - Nitrogen (passivation against reoxidation)
- Optional Gas
  - Oxygen (oxidizing chemistry)

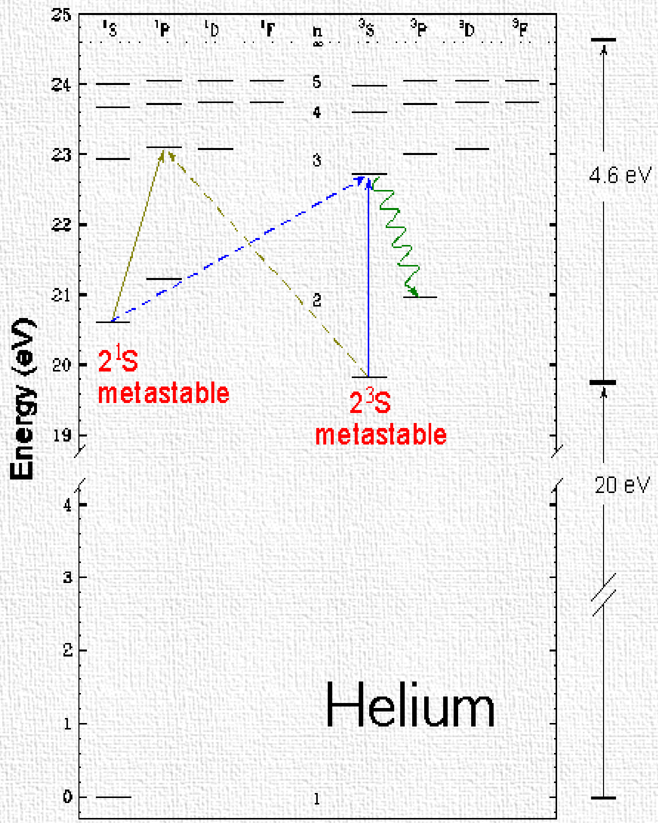






Quantum Energetics Activate Surface Reactions

- Helium (our 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 RF plasma), 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.
- This is somewhat analogous to the surface activation that occurs in R.I.E., except there is essentially ZERO kinetic energy transfer occurring, and therefore, zero kinetic (bombardment) damage to the substrate.

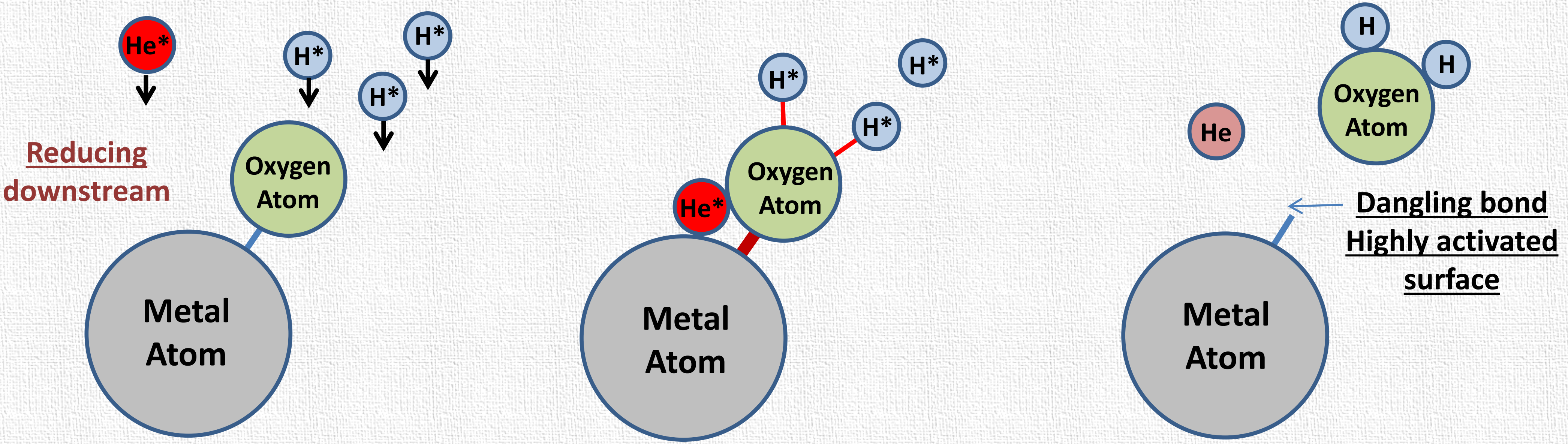


This is highly desirable for preparing the surfaces of sensitive semiconductor structures.

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

Quantum Energetics Activate Surface Reactions

Reactions with Oxygen (Oxides) with Reducing Chemistry

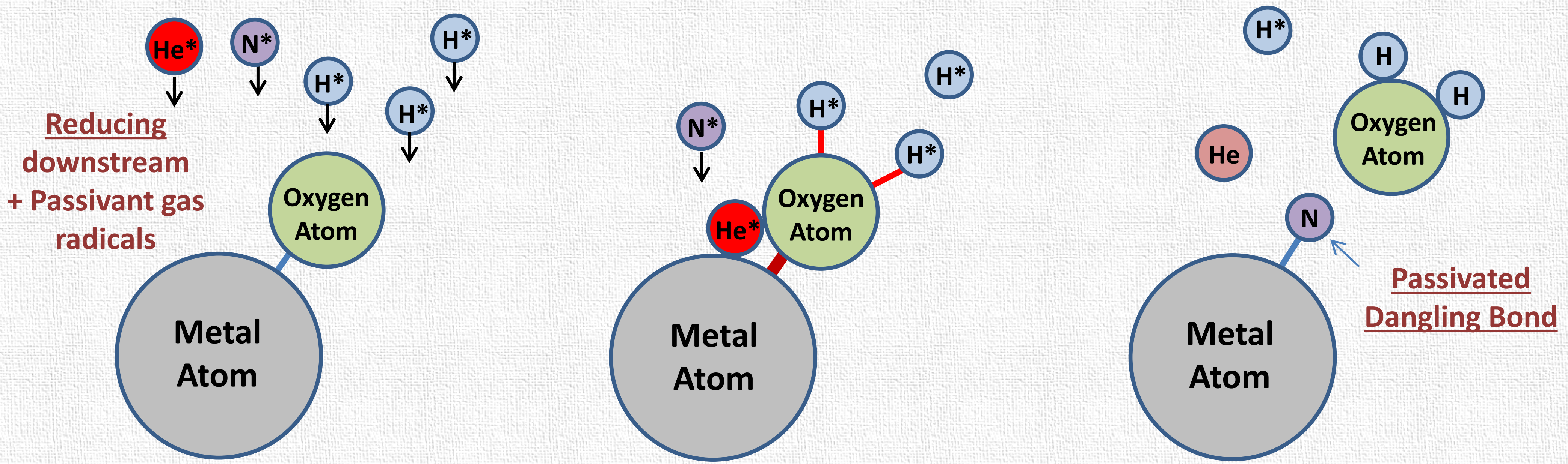


- The downstream gas flow contains Hydrogen radicals (highly reactive species) and metastable helium atoms which provide approximately 20eV of quantum energy directly to the substrate surface. This energy helps to activate chemical reactions, for example, two H* atoms reacting with an oxygen atom attached 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.

Quantum Energetics Activate Surface Reactions

Other gasses can be used to passivate dangling bonds against re-oxidation

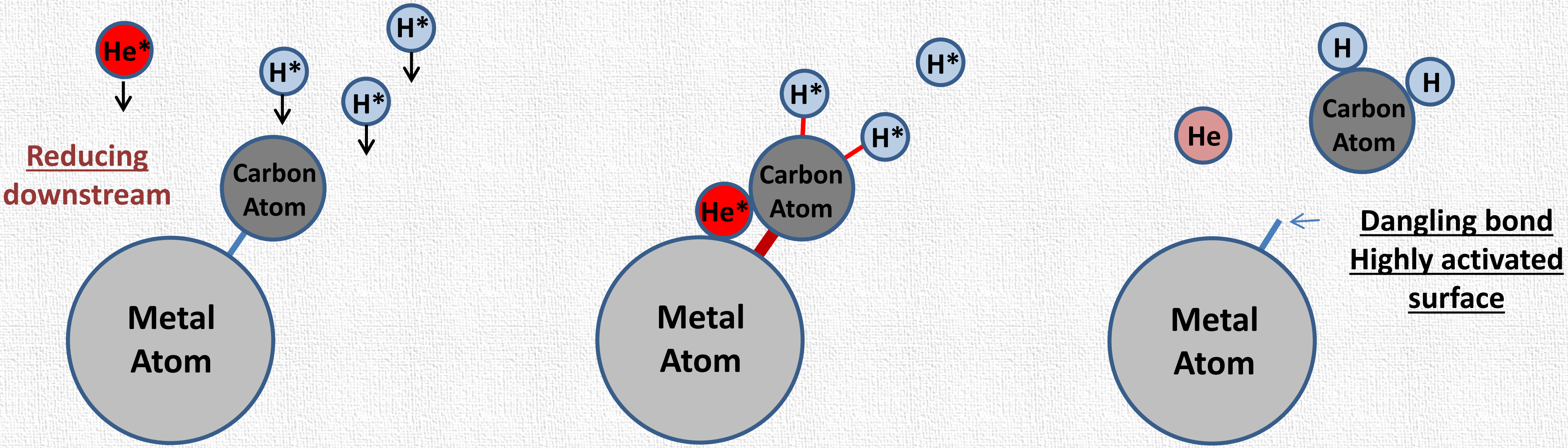


- Adding Nitrogen to the Atmospheric Plasma supplies N* radicals to occupy dangling bonds and inhibit re-oxidation.

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

Quantum Energetics Activate Surface Reactions

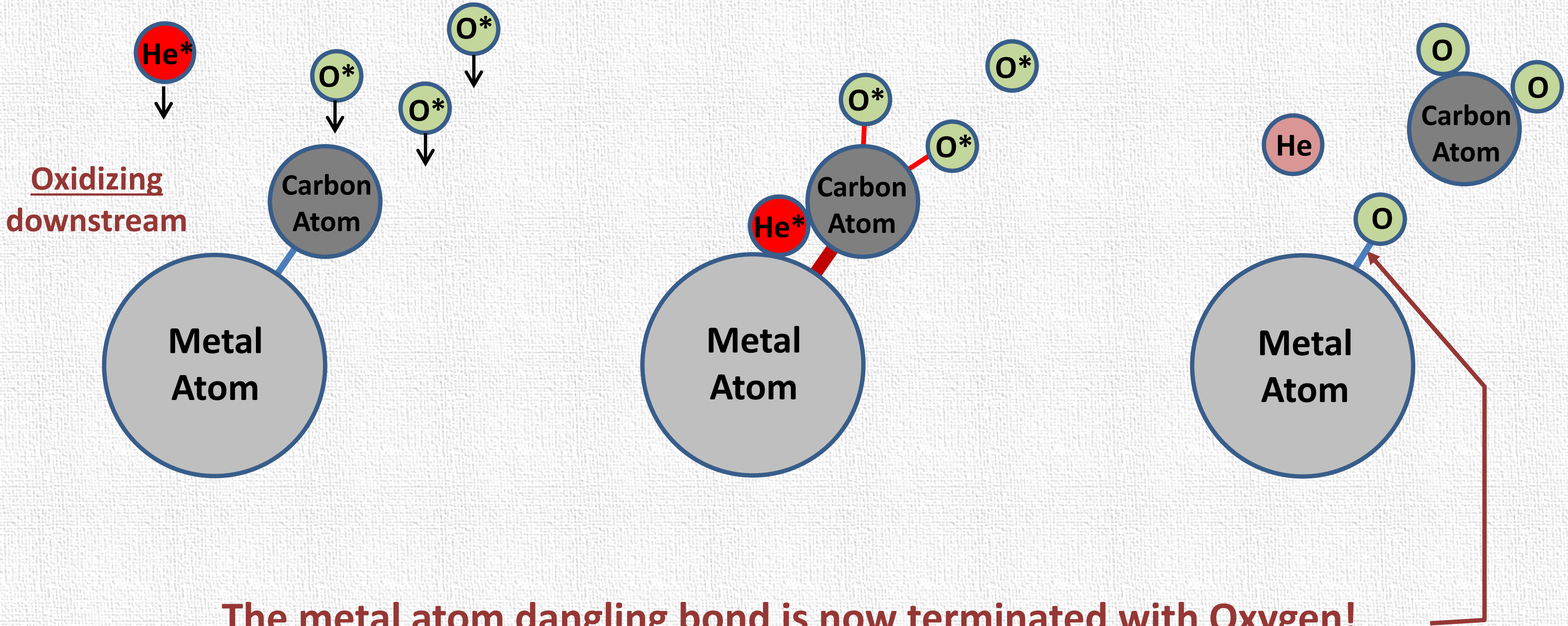
Similar reactions on Carbon (organics) with Reducing Chemistry



- The flow of downstream gas from the atmospheric plasma head sweeps all room air from the reaction region at the substrate surface.
- Reducing reactions are used to remove carbon, Hydroxyl (OH), and other contaminants from the substrate surface.

Quantum Energetics Activate Surface Reactions

Similar Reactions On Carbon (Organics) with Oxidizing Chemistry



The metal atom dangling bond is now terminated with Oxygen!

Possibly a method to control oxidation stoichiometry: *Passivation!*

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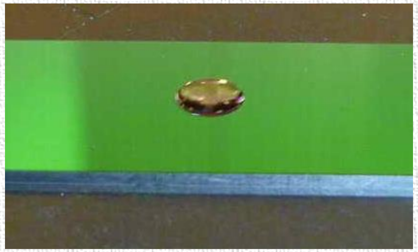
SURFACE ACTIVATION

Surface Activation with Ontos

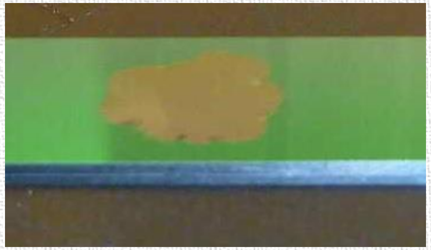
Pdf: Click for video on line

- Surface energy is a critical parameter for all types of aqueous and adhesive processing.
  - Wet etching.
  - Plating.
  - Rinse/clean.
  - Soldering.
  - Adhesives.
  - Evaporation
  - Sputtering
  - MBE
  - ALD
  - MOCVD
- Surface energy measurement (water droplet contact angle):



Example: SiO_2

Before Ontos → After Ontos



Note: Sample diced after deposition and exposed to the risk of organics contamination (storage)

High contact angle –
- Lower surface energy
- Poor wetting, Low adhesion
- Poor cleaning efficiency
- Inhibited Bonding

Low contact angle –
- High surface energy
- Best wetting, Best adhesion
- Best cleaning efficiency
- Intimate Atomic Bonding

- Ontos has provided successful surface activation of: II-VI's, III-V's, Si, SiO_2, Si_3N_4, photoresist, FRB, resins, polymers, Cu, In, Ni, Au, Ag, Al, Sn, SnAg, Ti …

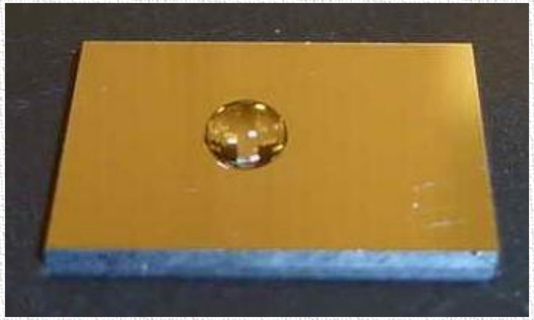
Surface Activation with Ontos (Examples 1/3)

SnAg

untreated

After Ontos

Nickel



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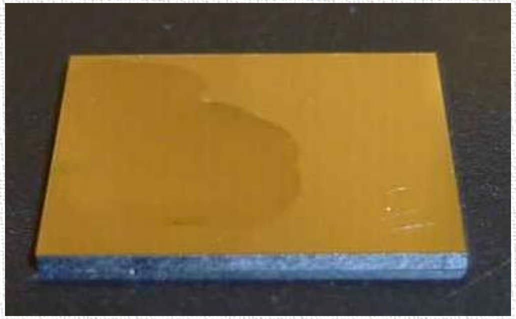
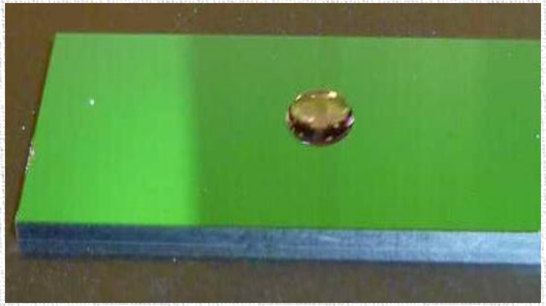


After Ontos

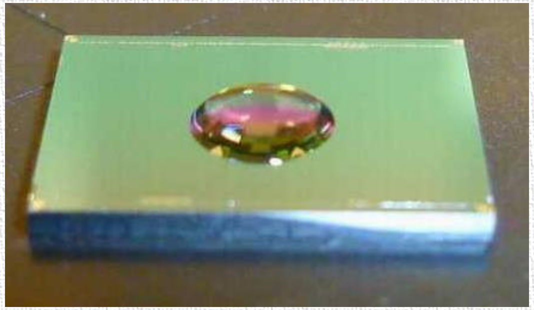
SiO_2



untreated

After Ontos

Si_3N_4



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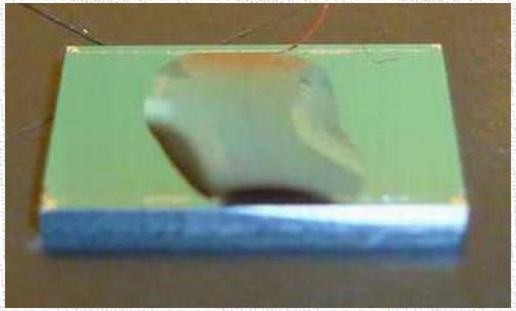


After Ontos

Note: All samples have been diced after deposition and exposed to the risk of organics contamination (storage)

Surface Activation with Ontos (Examples 2/3)

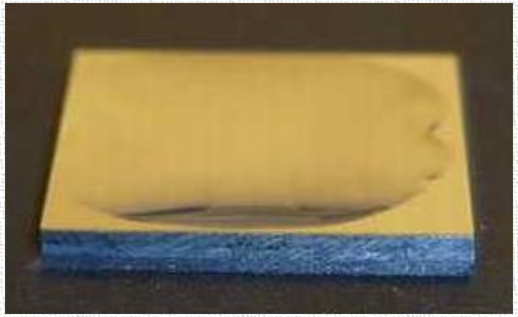
Copper

untreated

After Ontos

Aluminum

untreated



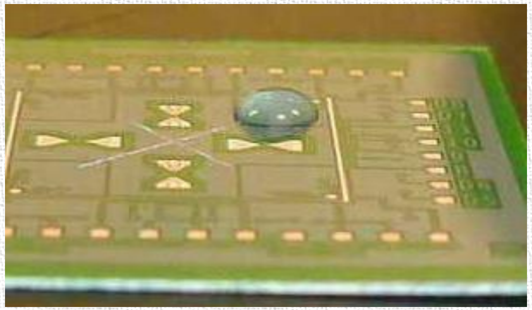
After Ontos

Photoresist

untreated

After Ontos

Composite



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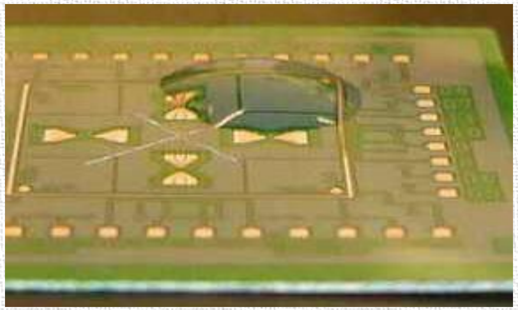
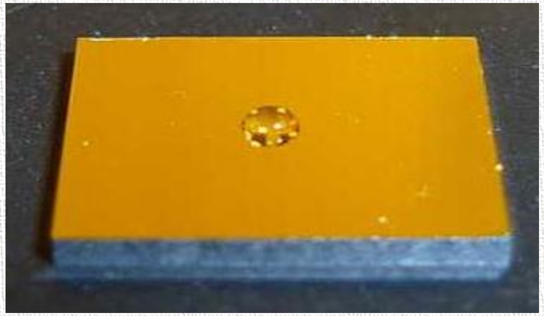


After Ontos

Note: All samples have been diced after deposition and exposed to the risk of organics contamination (storage)

Surface Activation with Ontos (Examples 3/3)

Gold



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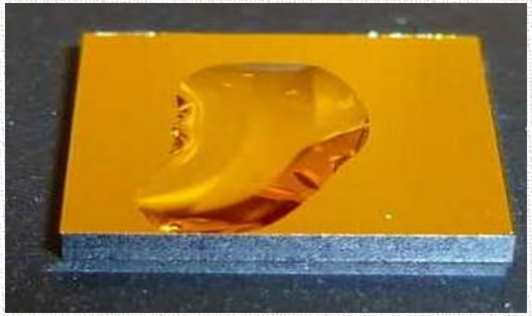


After Ontos

Tin

untreated

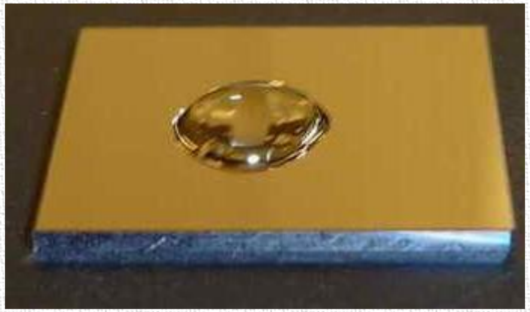
After Ontos

Indium

untreated

After Ontos

Titanium



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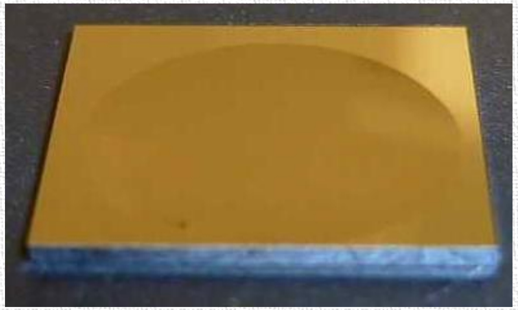


After Ontos

Note: All samples have been diced after deposition and exposed to the risk of organics contamination (storage)

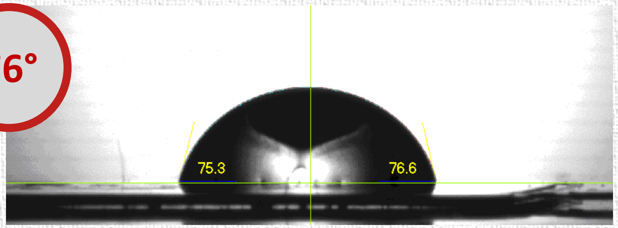
ONTOS Equipment Systems

Persistence of the Activation

Gold

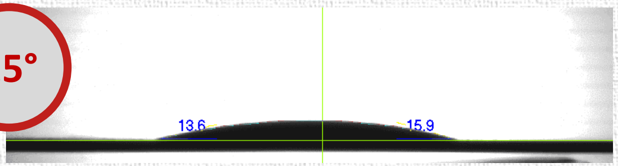
Before Ontos

76°



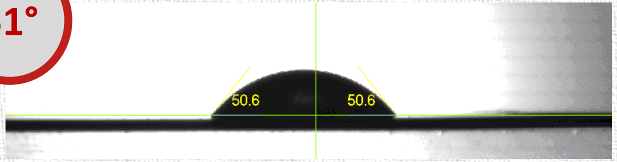
After Ontos

15°



After Ontos + 6 h

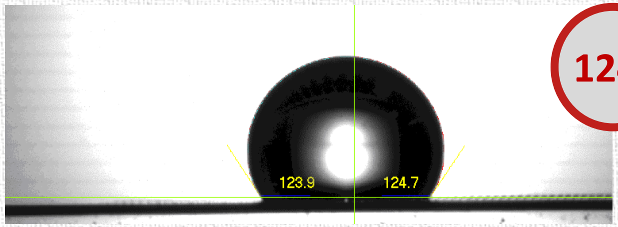
51°



Polyimide

Before Ontos

124°

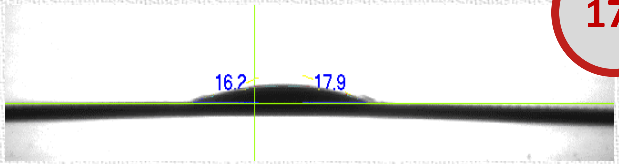


After Ontos

5°

After Ontos + 6 h

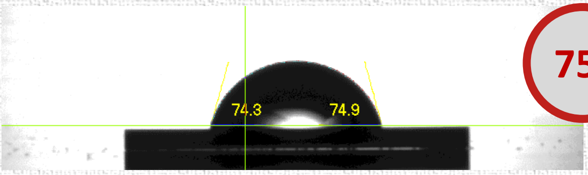
17°



Silicon

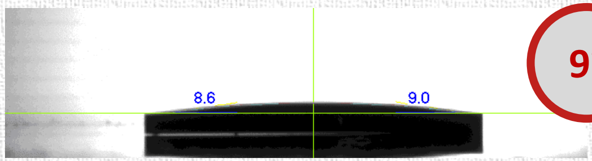
Before Ontos

75°



After Ontos

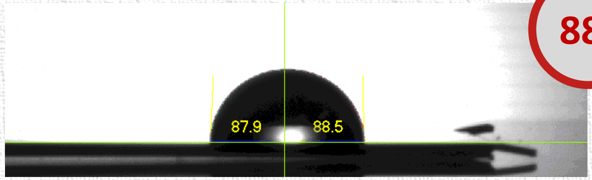
9°



Silver

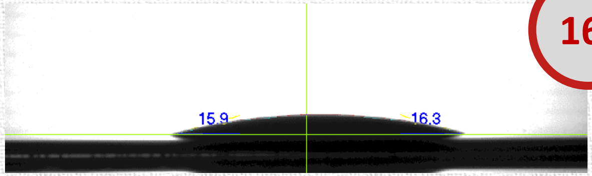
Before Ontos

88°



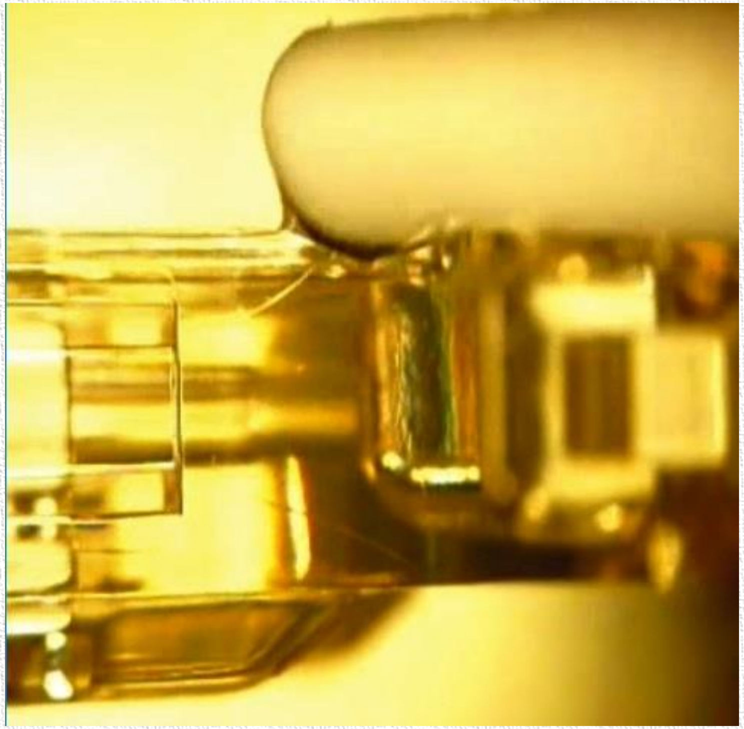
After Ontos

16°



Ontos oxidizing chemistry improves significantly the wettability of a Pacemaker module made of Tecothane (hydrophobic)

Untreated



No wetting

After Ontos: Single scan, oxidizing chemistry

Improved wetting

ONTOS
Equipment Systems

SOME APPLICATIONS IN SEMICONDUCTOR MANUFACTURING

Mainstream Semiconductor Applications

Front-End

- Wafer Clean:
  - Incoming
  - Epitaxy Prep
  - PR Residue Strip
  - Chemical Residue Strip
- Photolithography:
  - Adhesion Promoter
  - Descum Pattern
- Pre-wet For Aqueous Processes.
- Deposition Prep:
  - Final surface clean
  - Activation For Thin Film Adhesion
- RDL:
  - Plating base adhesion
  - PR descum
  - Pre-wet for plating

Back-End

- Plating prep for bumping.
- Direct bond: C2C, C2W, W2W.
- 3D IC Chip Stacking.
- Flip Chip Bump Prep.
- Capillary Underfill Enhancement.
- Adhesives Enhancement.
- Pre-Wire Bond clean.
- Pre-encapsulation surface activation.

ONTOS Equipment Systems

Specific Applications in Semiconductor Manufacturing

1. Wafer Clean Up
2. Photoresist Descum, Photoresist Activation
3. Preparation for Plating over Patterned Photoresist
4. Various organic materials removal
5. General Aqueous Processes
6. Dielectric Wet Etch
7. Metal Lift Off
8. Passivation of Delicate Surfaces
9. Photomask/Stamp Cleaning
10. Metal-to-Metal Bonding
11. Surface Activation: Preparation before Deposition, Capillary Underfill, Die Attach, Adhesive Process, etc.

1. Starting Wafer Cleanup

- What's on YOUR starting wafer?
  - Thin organic residue from polishing,
  - Chemical residue from etching,
  - Uncontrolled surface sub-oxides,
  - Adsorbed water and hydroxyls,
  - Organic contamination from packaging, handling, incoming inspection.

- <u>Be sure you are starting with a "clean slate"</u>
  - Ontos removal of atomic-scale contaminants from the wafer surface.
  - Passivation of the surface against re-gettering of Oxygen, Carbon, H_2O, etc.
  - Surface activation of the wafer for subsequent processes.
  - Ideal for epi growth, implant, diffusion, passivation, …

2. Photoresist Descum and Activation

Improve the yield of Photoresist-patterned processes

- Ontos removal of photoresist residue from previous mask steps
  Replace Oxygen Ash, UV Ozone.

- Descum of new PR pattern: Get excellent wetting
  Replace Oxygen Ash (which does not activate and alters linewidth).

- Surface activation of the photoresist for subsequent processes:

2. Photoresist Descum, Oxidizing Or Reducing Chemistry

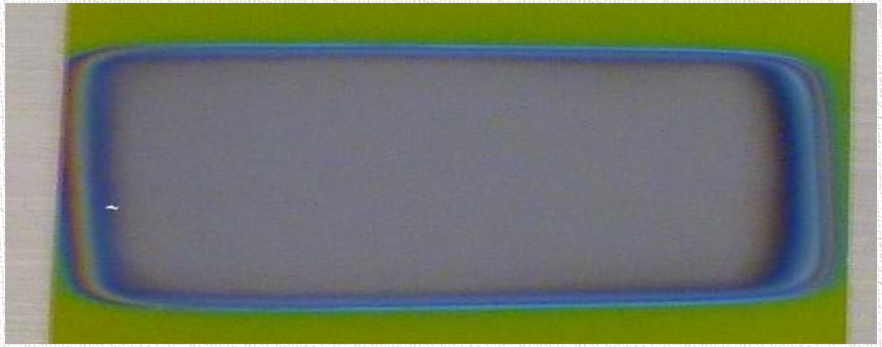
Ontos Atmospheric Plasma is uniquely suited to give the choice of Oxygen-based or Hydrogen-based chemistry.

- When oxidation of the underlying substrate is not a concern, Oxygen chemistry in Ontos can quickly strip Photoresist residue at room temperature.
  - Examples: descum over SiO, SiO_2, Si_3N_4

- When oxidation of the underlying substrate is a concern, Hydrogen chemistry can strip Photoresist residue at room temperature – and simultaneously remove oxidation instead of growing it.
  - Examples: Descum over Ni, Sn, Cu, Ag, Au (yes Au does oxidize – it is a thin layer, but it is there and can impede very low currents and bonding).

2. Descum of photoresist residue (Oxygen Chemistry)

- Ontos Atmospheric Plasma produces a very high density of Oxygen radicals – up to ~5.10^{18}/cm3.
- At high power and low scan speed, Ontos can remove entire films of photoresist, even at room temperature.
- Substrate heating increases removal rate.
- In descum mode, high scan rates and or lower power can be used to remove thin PR residue from a pattern with minimal change in PR linewidths.
- Process time to descum a 200mm wafer: approximately 3 minutes.
- Excellent process to use when oxidation of exposed surface is not an issue.



300 Nm of i-line photoresist removed with Ontos AP Oxygen strip – room temperature

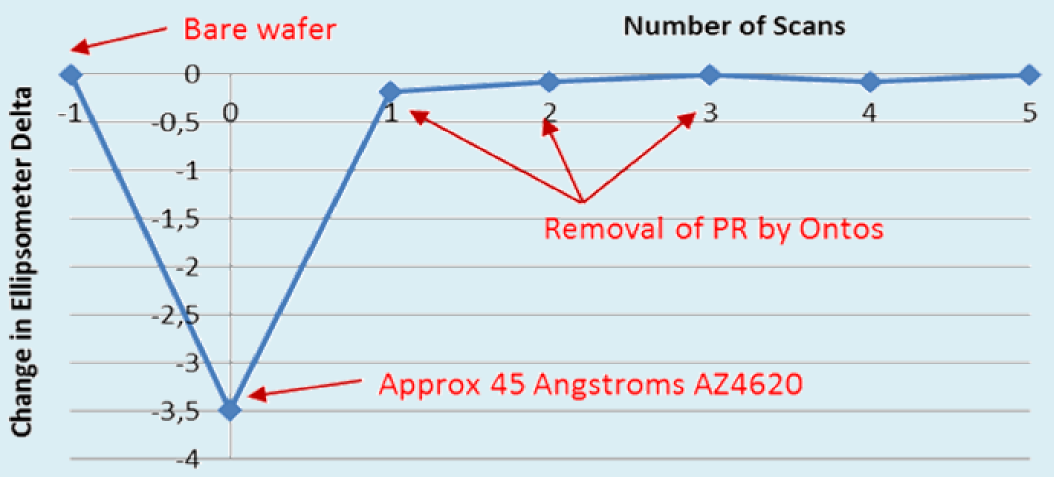
80Nm of amorphous carbon removed with Ontos AP Oxygen strip – room temperature

2. Descum of photoresist residue

- In semiconductor processing there exists a slight residue of photoresist material ("scum") at the bottom of a developed-out resist pattern.
- Oxygen ashing in a vacuum system is most often used to remove this scum.
- Atmospheric Plasma takes a different direction by using reducing chemistry (Hydrogen-based excited species) to remove post-develop photoresist scum.
- It has the advantage of **reducing the oxide on the exposed metallic surface** enabling a better adhesion for subsequent treatment

  (i.e.: Metal deposition for bumping).

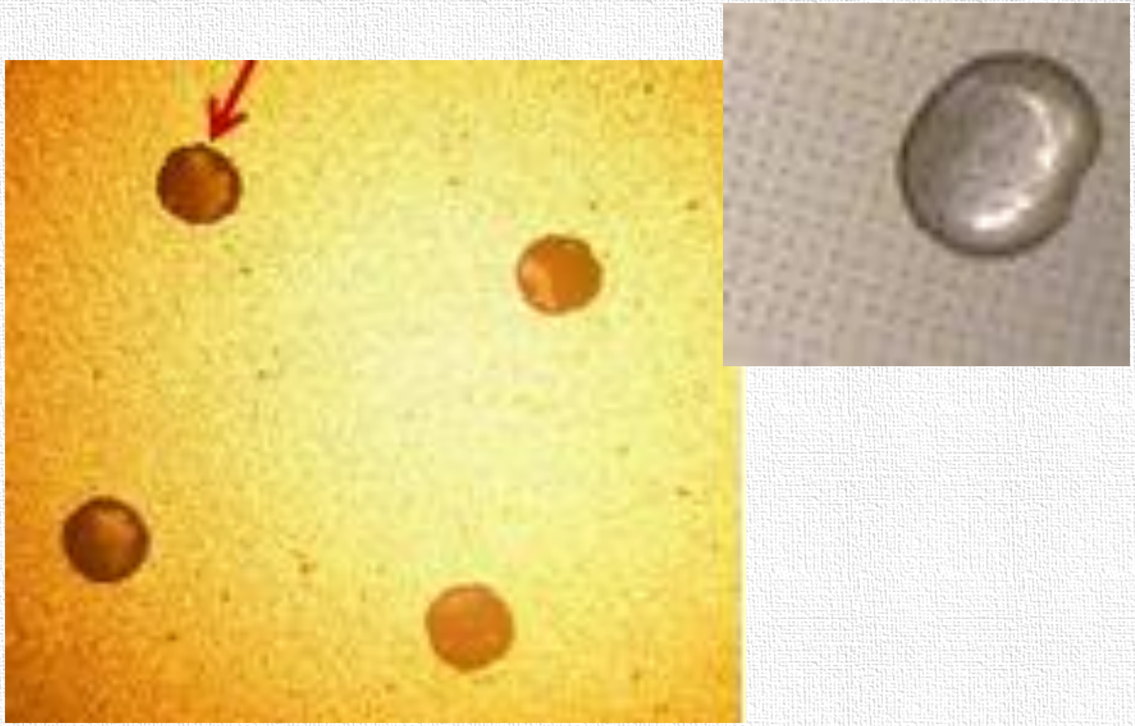
AZ4620 residue response to Ontos $He/H_2/N_2$

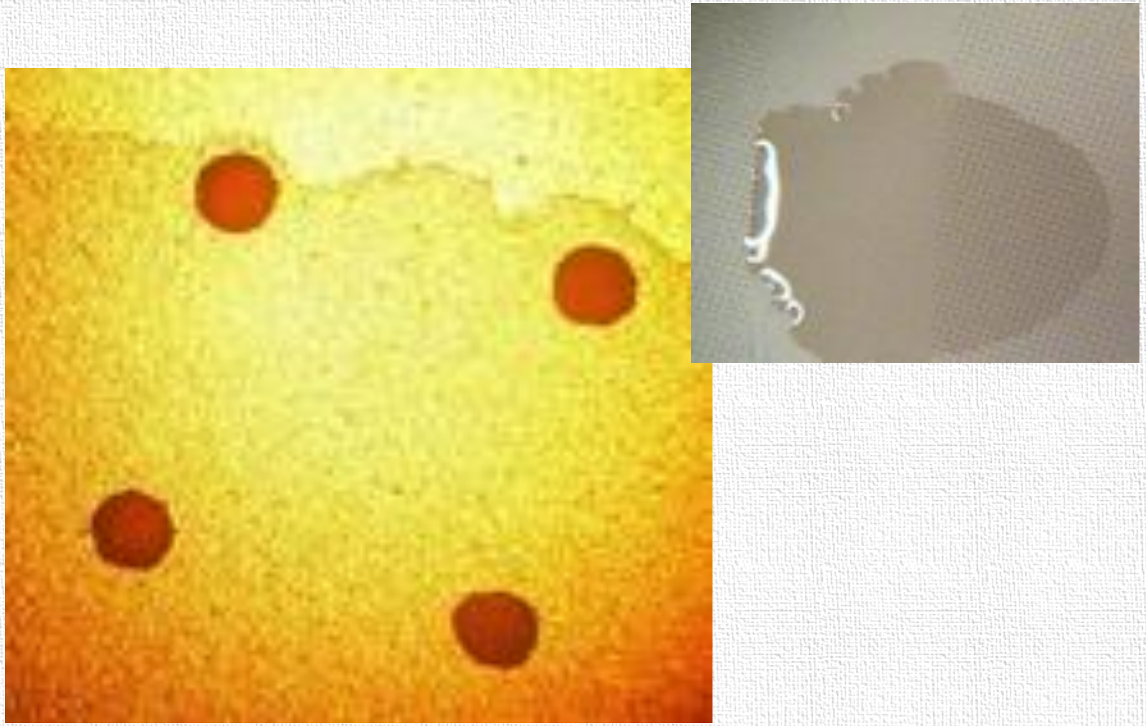


SiO_2-coated silicon wafer was over coated with a very dilute solution of positive photoresist (AZ4620) in acetone, and then dried on a hotplate.

2. Activation of Photoresist for Vias Wetting

- Photos: Polyimide on Silicon with laser-ablated apertures (diameter ~100µm and 800µm deep).





<u>Without</u> Atmospheric Plasma

- Entrapped air prevents aqueous solution from entering small features.

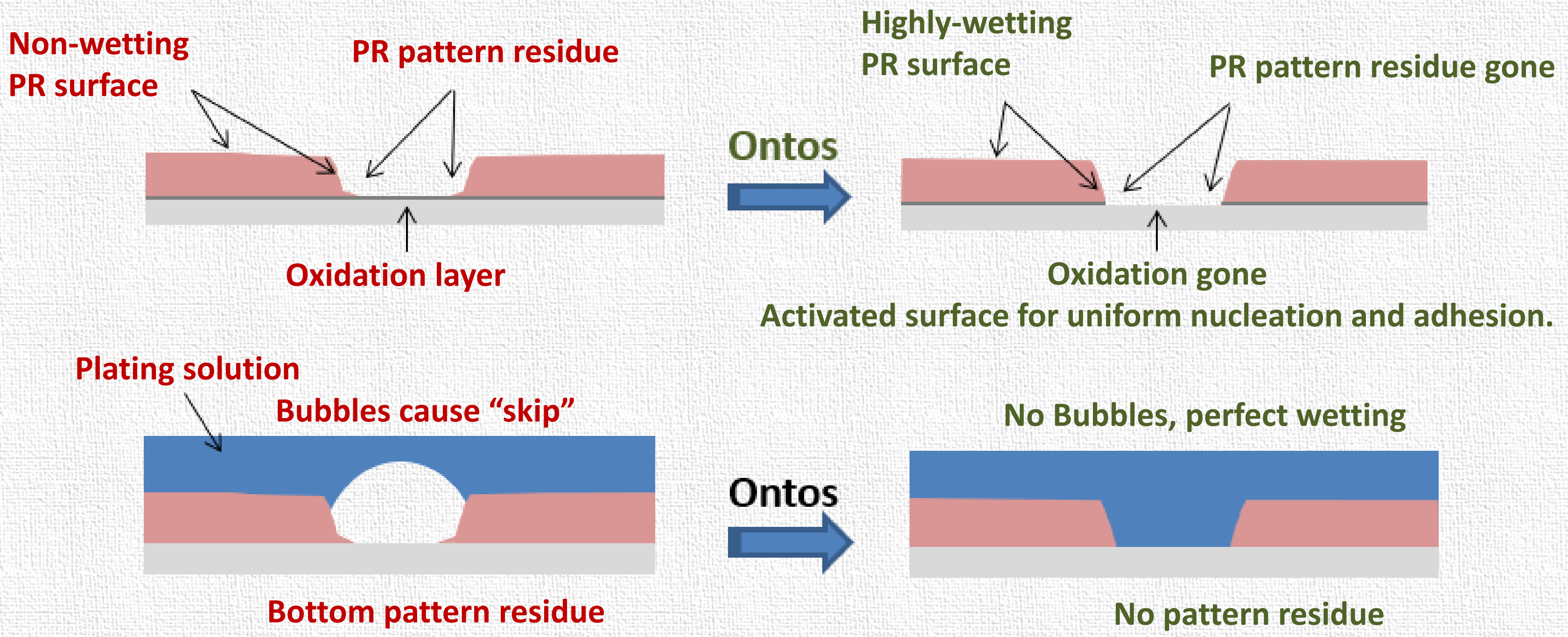
<u>With</u> Atmospheric Plasma

- Surface-activated material draws plating solution into smallest features.

3. Preparation for Plating

Use Ontos with **reducing** chemistry before plating

- Descum the PR pattern to remove bottom residue (**without Oxygen!**).
- De-oxidize the exposed plating base surface for uniform nucleation.
- Activate the plating base surface for maximum adhesion.



3. Preparation for Plating

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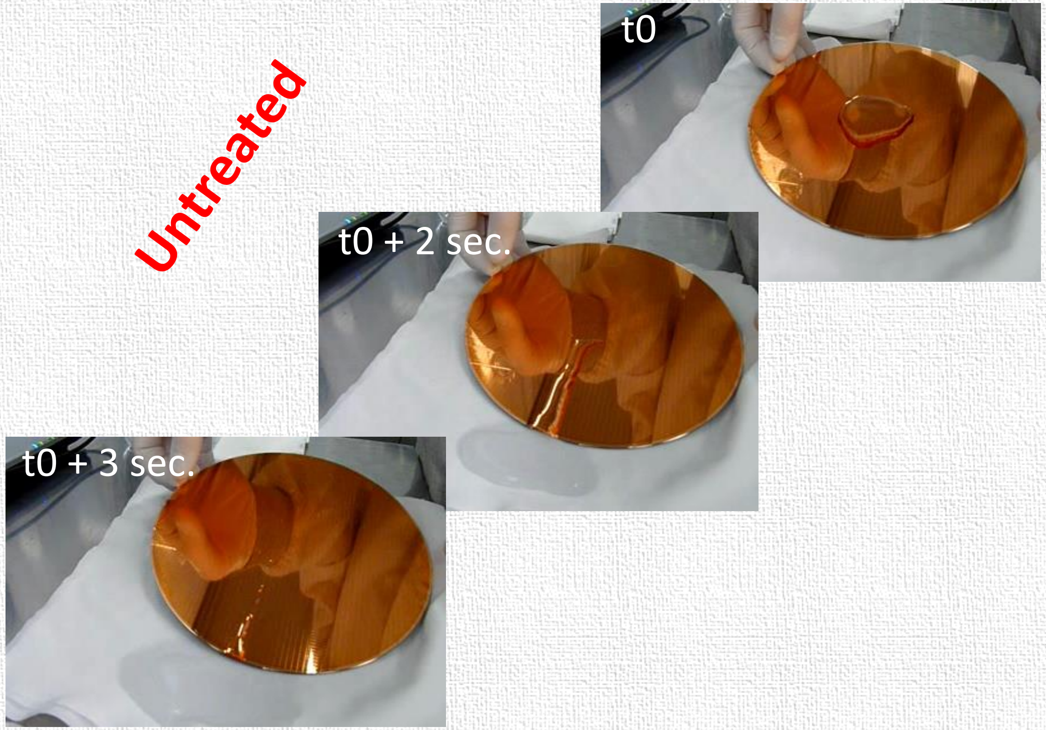
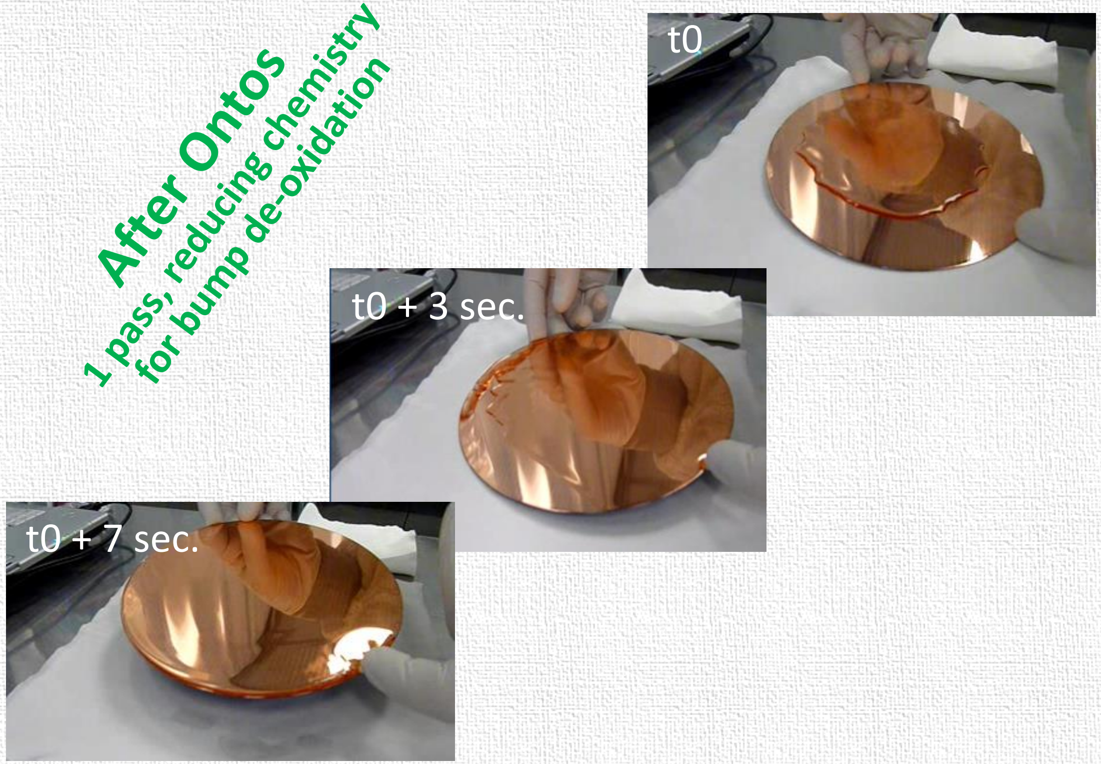
Positive PR over Cu plating base

Untreated



After Ontos
1 pass, reducing chemistry for bump de-oxidation



No wetting of Photoresist or metal pattern

- Process voids
- Non-uniformity
- Time control issues

Superb wetting of both Photoresist and Metal

- Wets smallest features
- Cross-wafer uniformity
- Timing consistency

4. Removal of various Organic Materials

- The Efficiency of the Ontos Atmospheric Plasma has been successfully demonstrated on the following Organic Materials, usually difficult to remove:
  - Polyimide,
  - Amorphous carbon,
  - Implanted photoresist.

- Entire films of Photoresist will probably take 30-60 minutes to remove from a 200mm wafer.

  However if only thin residue of photoresist (i.e. less than 100nm) this can be accomplished by Ontos quickly.

  Also, if only chips are being cleaned, Ontos can be much faster than plasma ash methods.

- These removal rates assume using substrate heating of up to 250°C.

  The Ontos system is not yet proposed with a substrate heater, but this could be quoted upon request.

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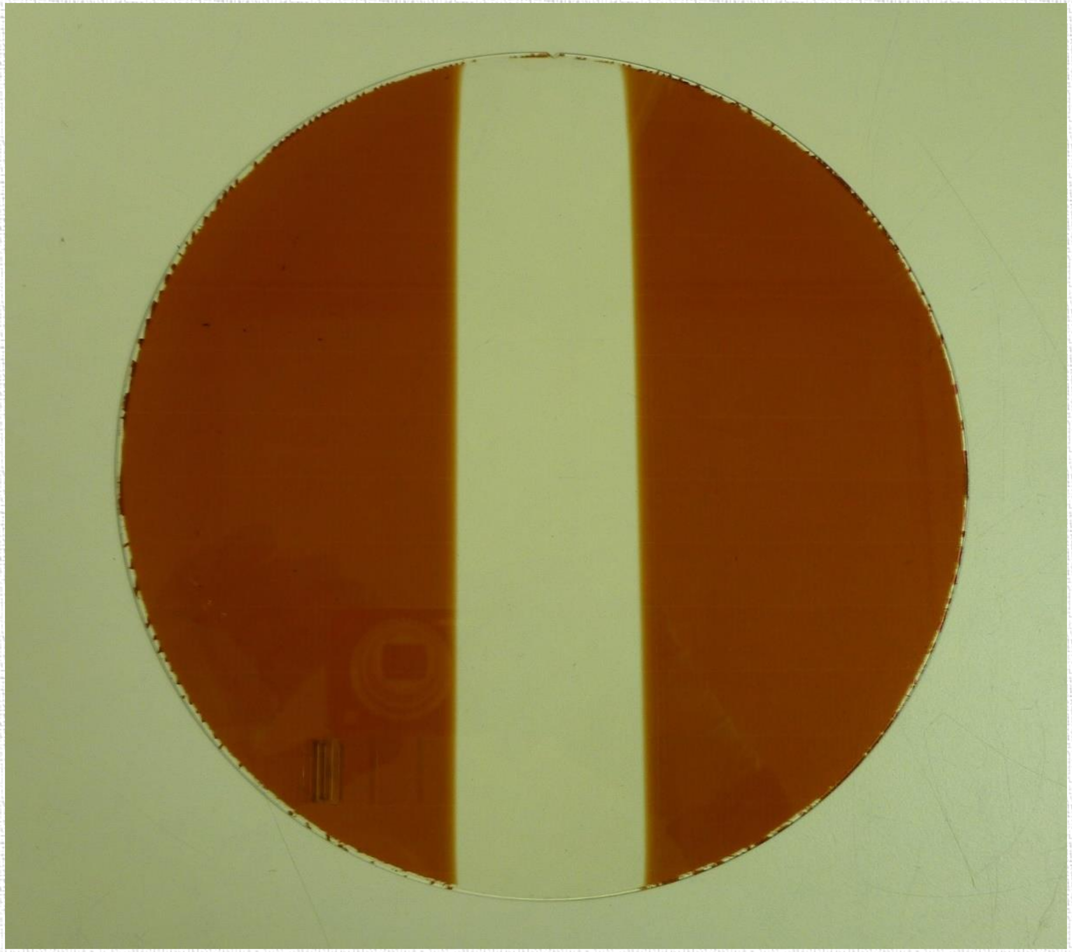
4. Polyimide on Glass Wafer



- Polyimide 10 micron thick on a glass wafer, was completely removed
- No substrate heat
- Single pass with scan rate of 0.5 mm/sec
- Helium + Oxygen Chemistry.
- This translates to clearing a 200mm wafer in approximately 53 minutes.
  (Plasma Head Aperture 25mm)

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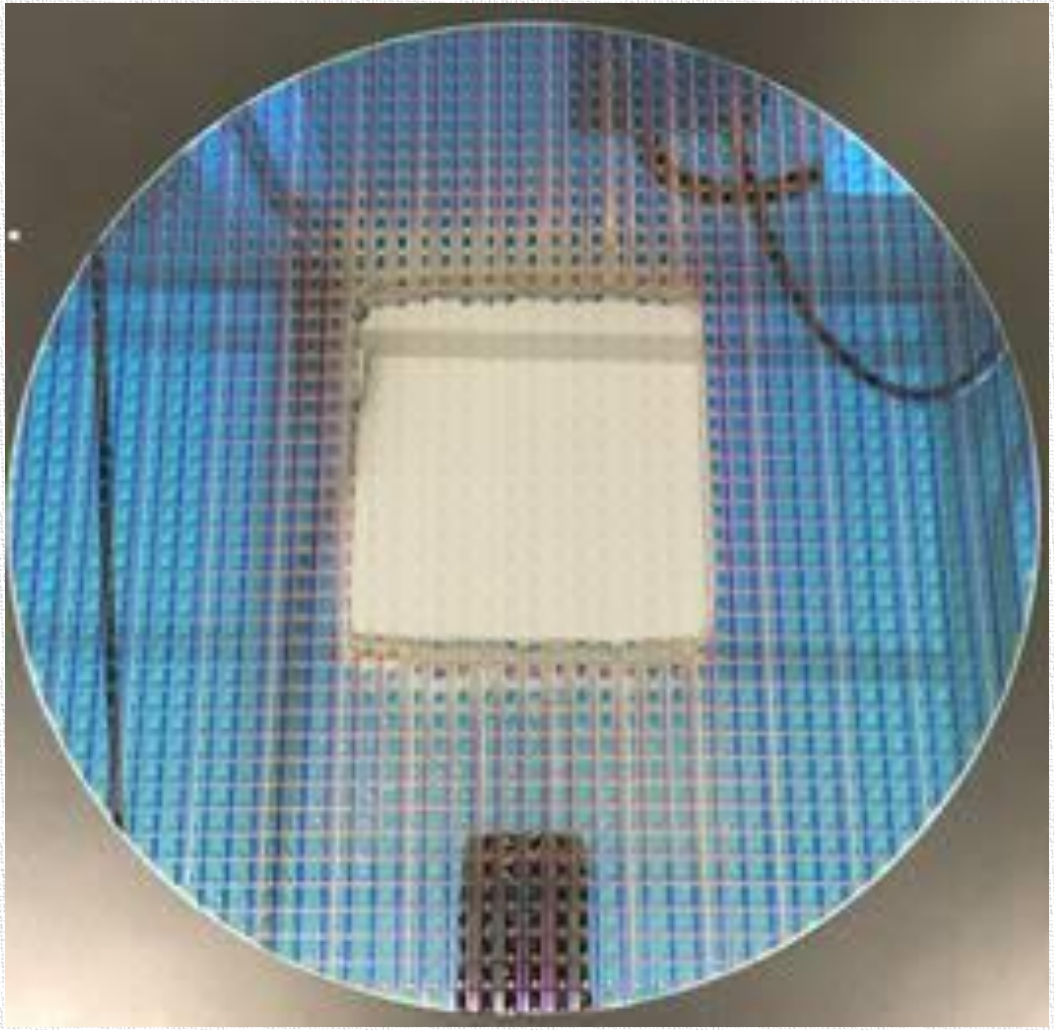
4. Implanted Photoresist on Processed Silicon Wafer



- Implanted Photoresist (~ 2000nm) on Silicon Wafer was completely removed
- Substrate Heated at 250°C,
- Single Pass at Scan Rate 1.0 mm/sec
- Helium + Oxygen Chemistry.
- This translates to clearing a 200mm wafer in approximately 27 minutes.
  (Plasma Head Aperture 25mm)

4. Implanted Photoresist on Bare Silicon Wafer

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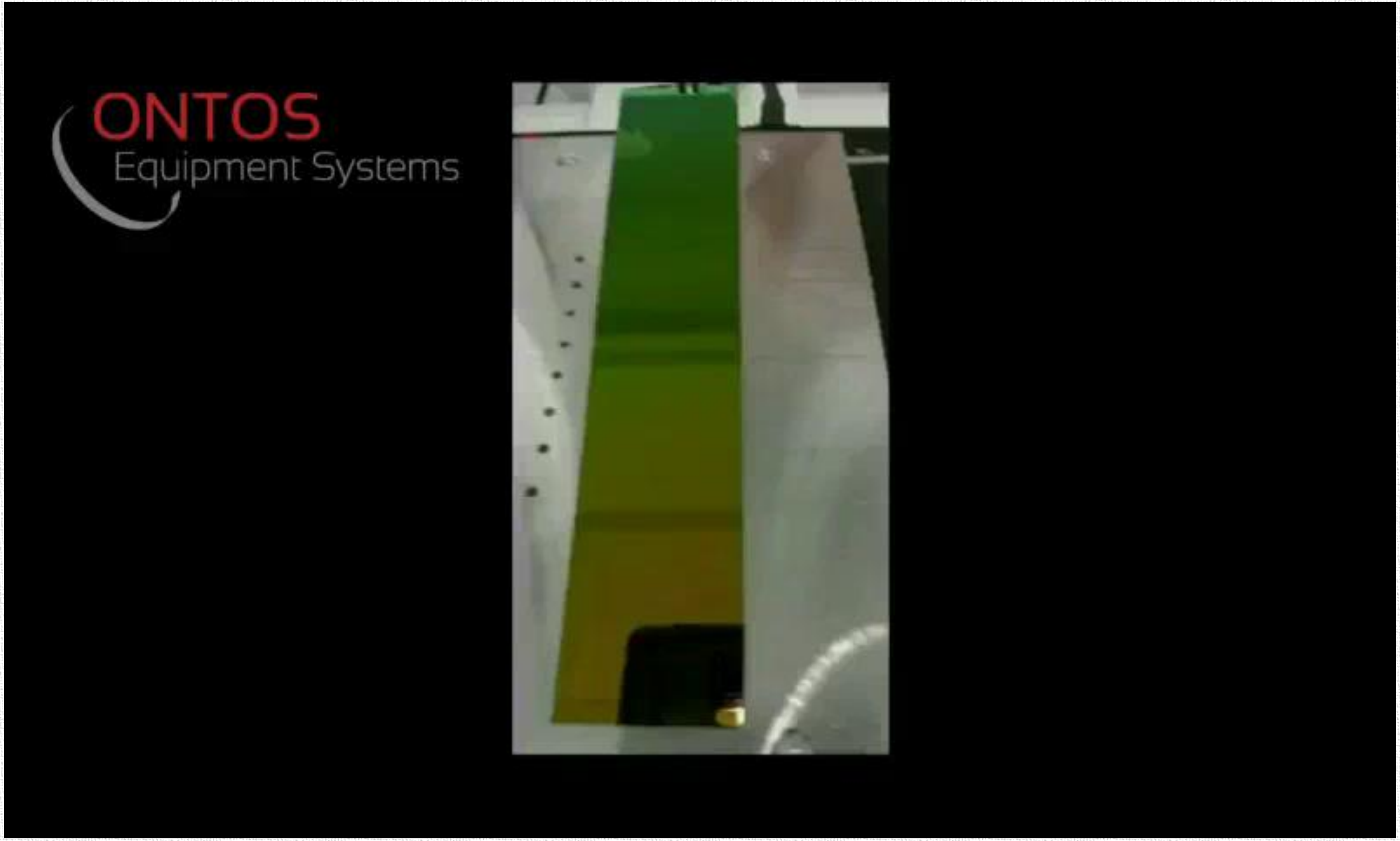
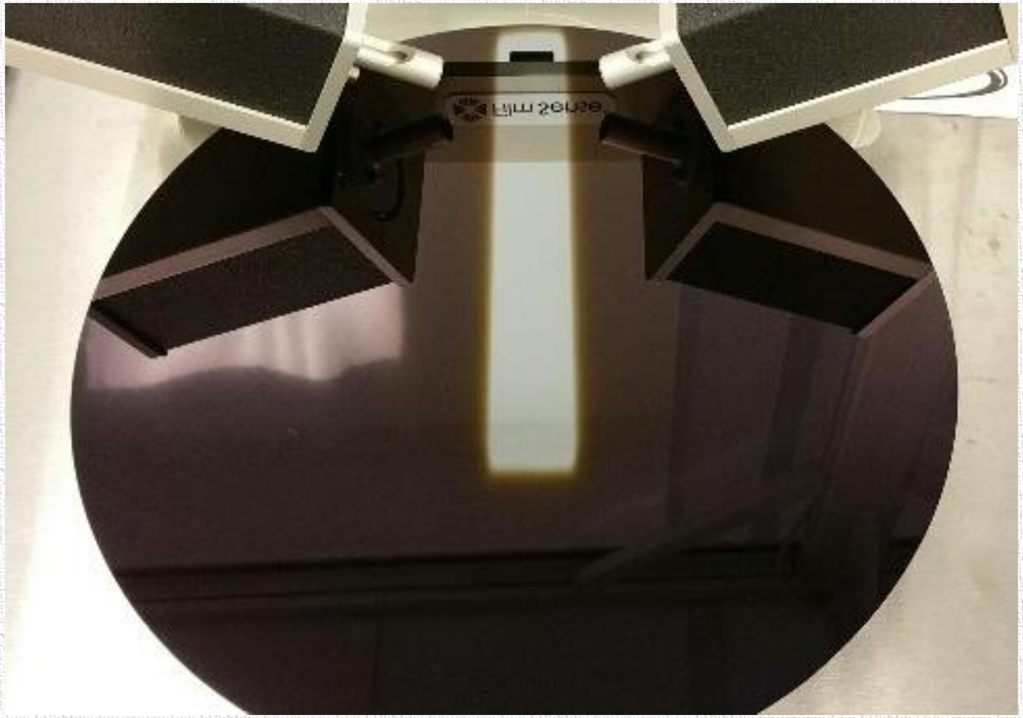


4. Amorphous Carbon on Silicon Wafer

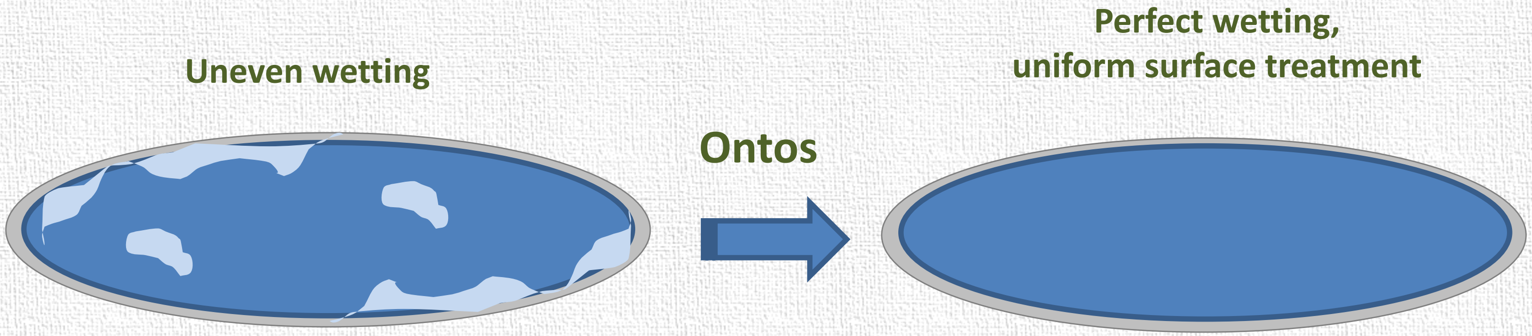


- Amorphous carbon (80 nm thick) on Silicon - completely removed
- Substrate at room temperature,
- One pass, scan rate 0.1 mm/sec,
- Helium + Oxygen chemistry.
- This translates to clearing a 200mm wafer in approximately 260 minutes.

  (If the substrate is heated to 200°C, the projected time to strip a 200mm wafer is approximately 20 minutes).

Improve uniformity, eliminate organic-induced non-wetting

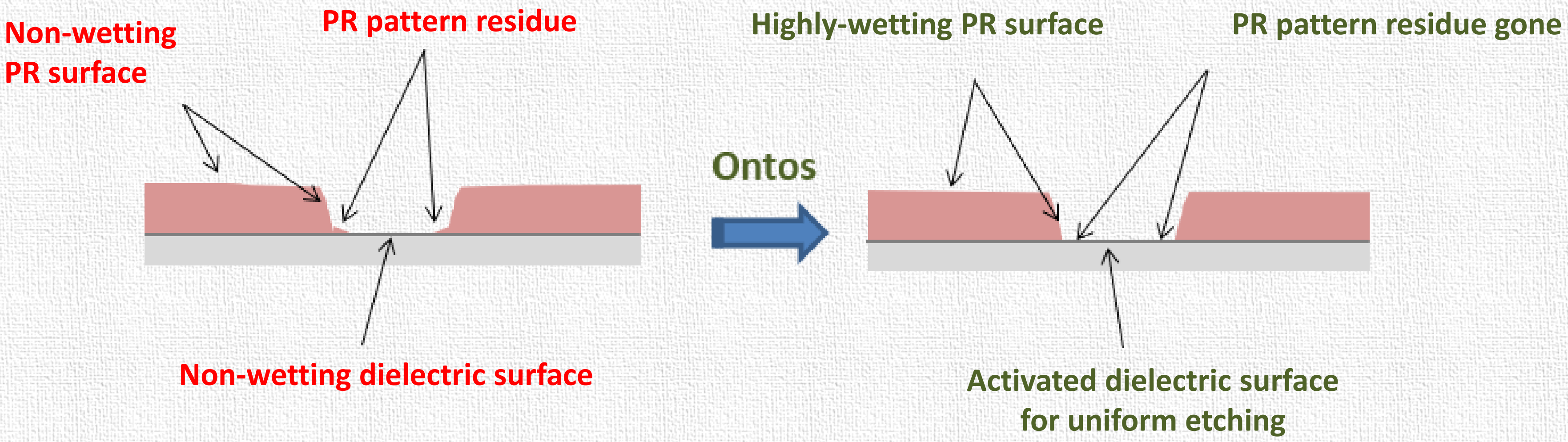
- Ontos removal of sub-oxide residue from wafer storage in atmosphere.
- Ontos removal of organic residue from wafer storage, handling.
- Surface activation of the wafer for perfectly uniform wetting



6. Dielectric Wet Etch

Use Ontos with **Oxidizing** Chemistry prior to wet etch

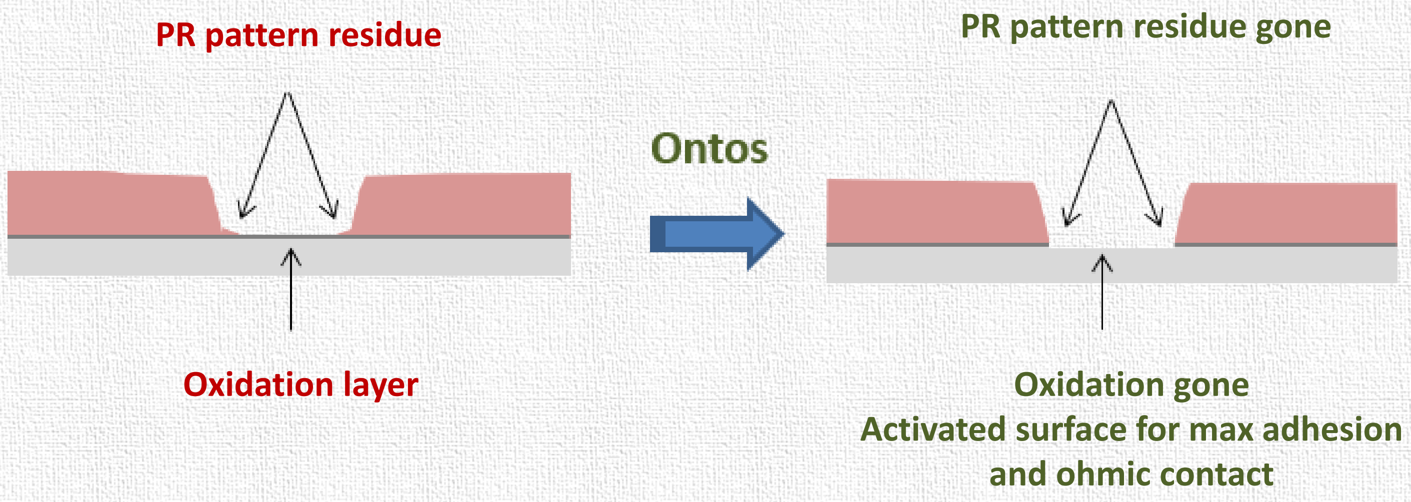
- Descum the PR pattern to remove bottom residue.
- Activate the surface of photoresist and dielectric for best wetting
  - Improves etching uniformity; no bubbles, no skips.
  - Reduces need to "over-etch" to clear small geometries.



Use Ontos with **Reducing** Chemistry Prior to Metal Deposition

- Descum the PR pattern to remove bottom residue (without Oxygen!).
- De-oxidize the exposed surface for better ohmic contact.

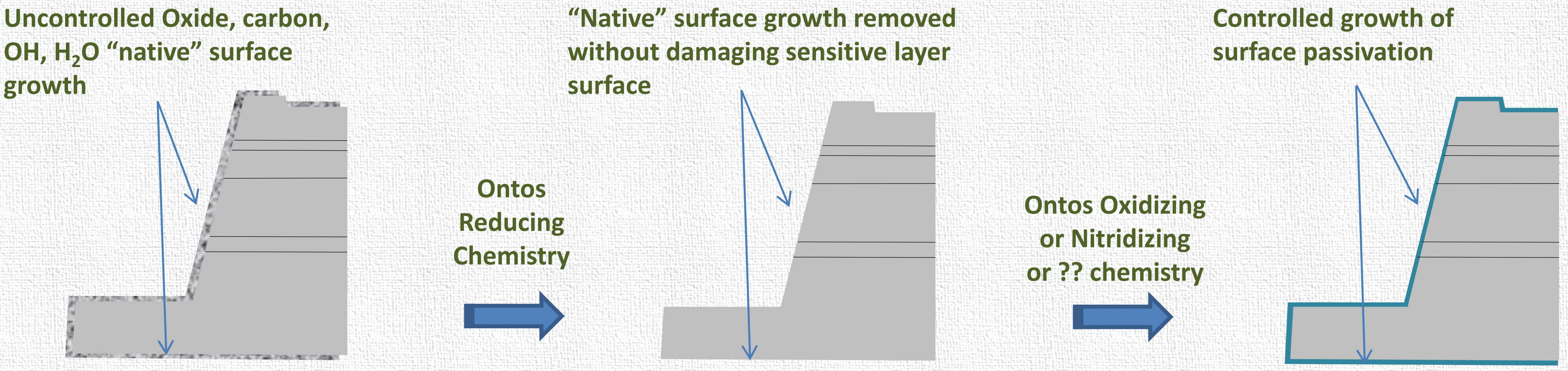
  Activate the contact surface to improve adhesion of new metal layer.



ONTOS Equipment Systems

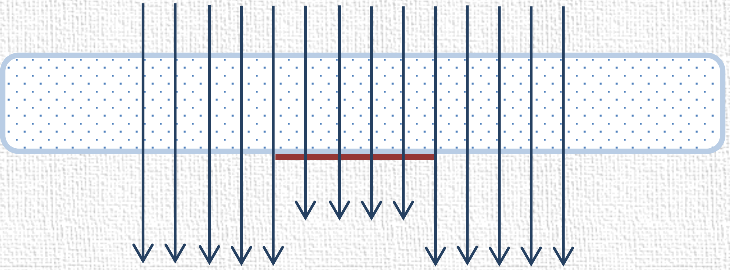
8. Passivation of Delicate Surfaces

- Ontos removes undesirable oxidation, organic contamination, creates a pristine surface **without** surface damage.
- Controlled passivation of the surface with Oxygen or Nitrogen or ??
  - Mesa sidewalls
  - Exposed junction edges
  - Detector backside surface flat-band adjustment, activated controlled surface for backside A-R coat.



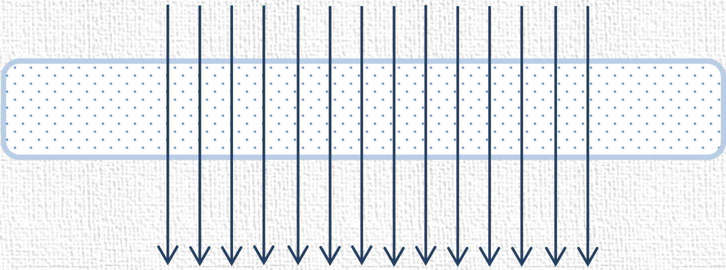
9. Photomask Cleaning

- Removes organic contamination without damaging sensitive mask materials. (safe for ALL masking materials, even EUVL and NIL)
- Enables extreme wetting for aqueous cleaning processes – spot-free.

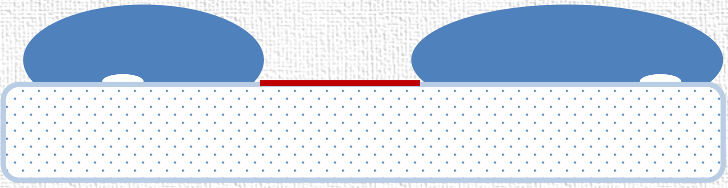


Slightest PR residue inhibits UV transmission causes uneven exposure

Ontos →



PR residue removed
Get uniform exposure



Slightest PR residue makes surface impossible to wet, poor wet cleaning results

Ontos →

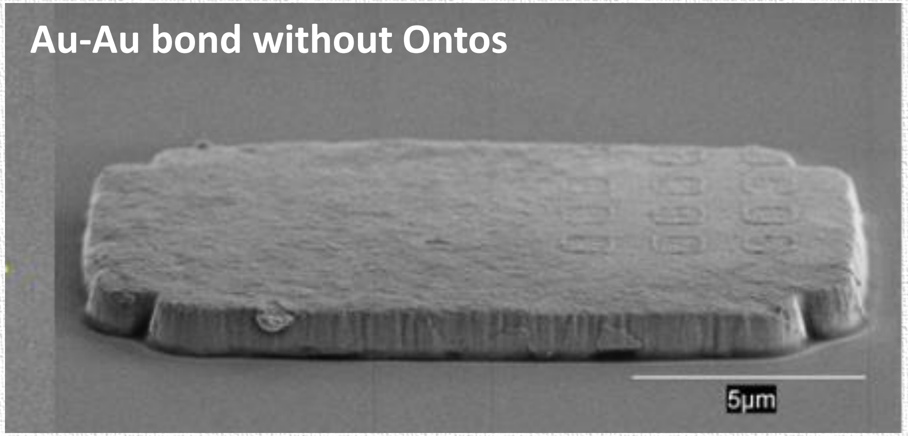
PR residue removed
Mask surface activated for uniform wet clean

10. Metal-to-metal Bonding

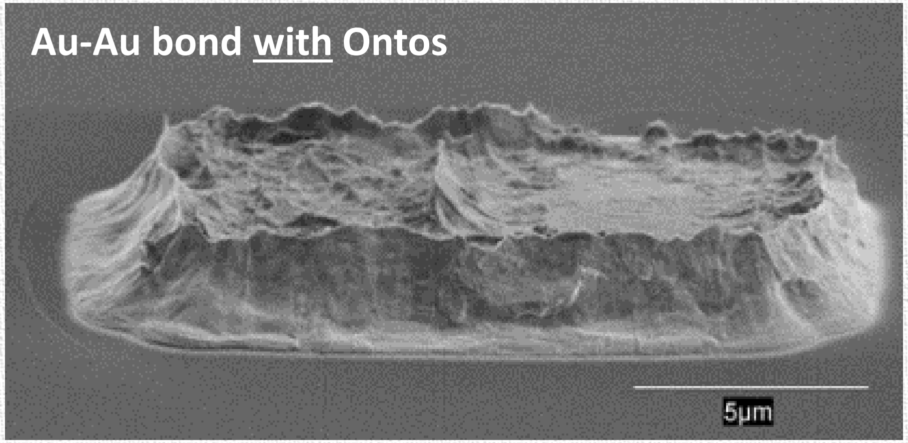
Ontos produces a pristine, activated surface for:

- **Direct Bonding:**
  - Semiconductor-to-semiconductor (at RT)
  - Oxide-to-Oxide (at RT)
  - Oxide-to-Nitride (at RT)
  - Oxide-to-semiconductor (at RT)

- **Metal-to-metal:**
  - Au – Au (as low as 100°C)
  - In – In (at RT) (see next page)
  - In – metal pad (at RT)
  - In – Ag (at RT)
  - SnAg – Cu (at 175°C)
  - SAC – Cu (at 175°C)
  - SAC – SAC (at 175°C)
  - … more



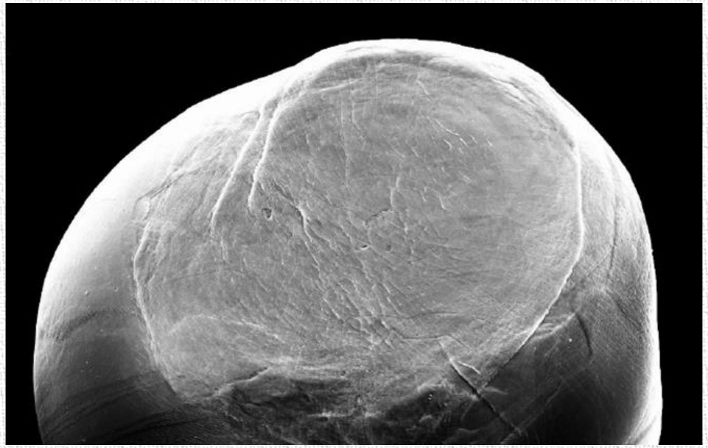
Gold bump after Pull Test (200°C)



10. Metal-to-metal Bonding (Indium Bumps)

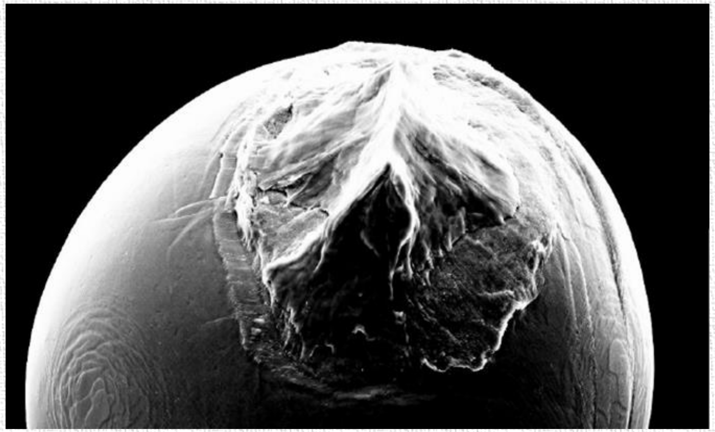
Indium bump to Indium bump (70µm bumps)

- No surface treatment.
- Room temperature compression (1g/bump)
- No post-bond reflow.
- Pull test shows Indium compression but zero adhesion



Indium bump to Indium bump (70µm bumps)

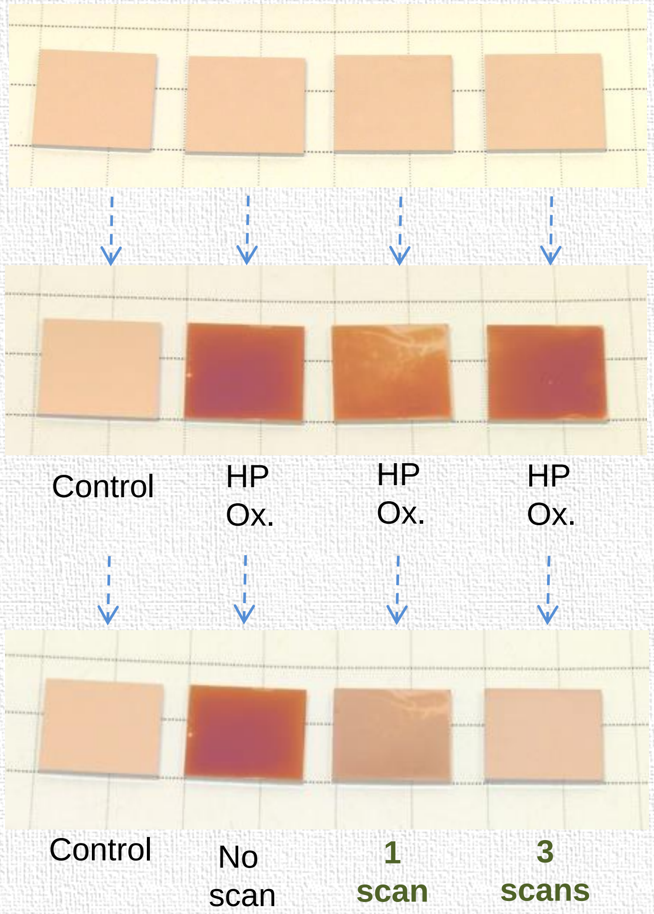
- Both surfaces Ontos-treated.
- Room temperature compression (1g/bump)
- No post-bond reflow.
- Pull test shows ideal tensile rupture of Indium.



10. Metal-to-metal Bonding (Copper 1/3)

Pdf: Click for video on line!

Removing Heavy Copper Oxide at Room Temperature



4 Cu/Si coupons out of the box

3 coupons hotplate oxidized at 150°C for 12 minutes (~ 400 Angstroms)

The Atmospheric Plasma reduces Cu Oxides at Room Temperature
3 scans returns Cu to native state.

Reduction of Cu oxides, CuO/Cu_2O, is accomplished by a combination of Hydrogen radicals (H*) and Helium metastables.

Oxygen is reduced from the surface of the Cu, the oxygen from below the surface sees a strong gradient which most probably causes Oxygen atoms to diffuse toward the surface region by a “vacancy-hopping” mechanism.

As the Oxygen atoms arrive at the surface, they are rapidly reduced to H_2O and swept from the surface by the gas flow.

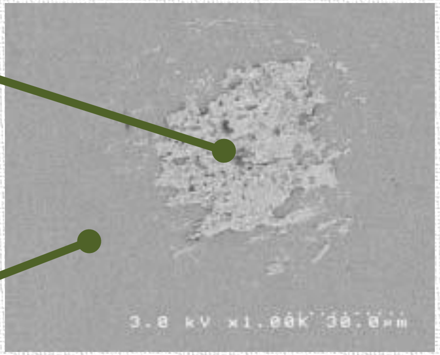
10. Metal-to-metal Bonding (Copper 2/3)

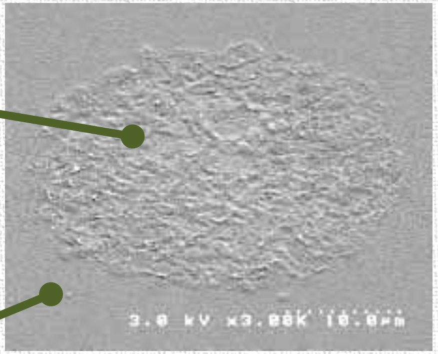
Bonding to Copper Treated with Ontos

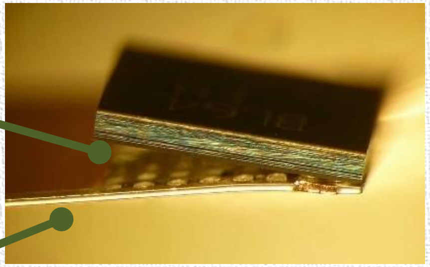
- **Indium to Copper**
  - Both surfaces treated.
  - Room temperature compression.
  - **No reflow**.
  - Shear test shows In bonded to Cu.

- **SnAg to Copper**
  - Both surfaces treated.
  - 185°C thermo-compression in air.
  - **No reflow**
  - Shear test shows SnAg bonded to Cu.

- **SAC to Copper**
  - Both surfaces treated.
  - 280°C thermo-compression in air.
  - Shear test shows SAC bonded to Cu.
  - Very strong adhesion, bent Cu substrate.







Passivation against Copper re-oxidation

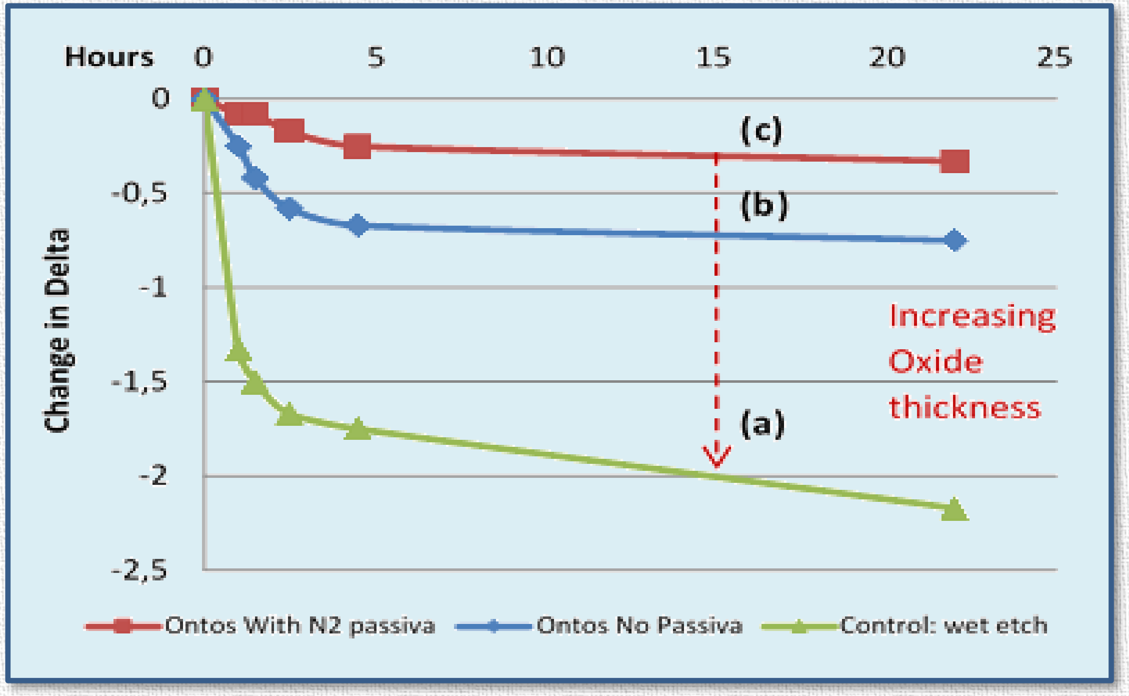
- With the addition of N* in the downstream from the atmospheric plasma, the de-oxidized Copper can be passivated to inhibit re-oxidation of the Copper with exposure to air.
- Graph shows the re-oxidation of Copper as a function of time for 3 different conditions:

a) Fresh clean copper with no surface treatment

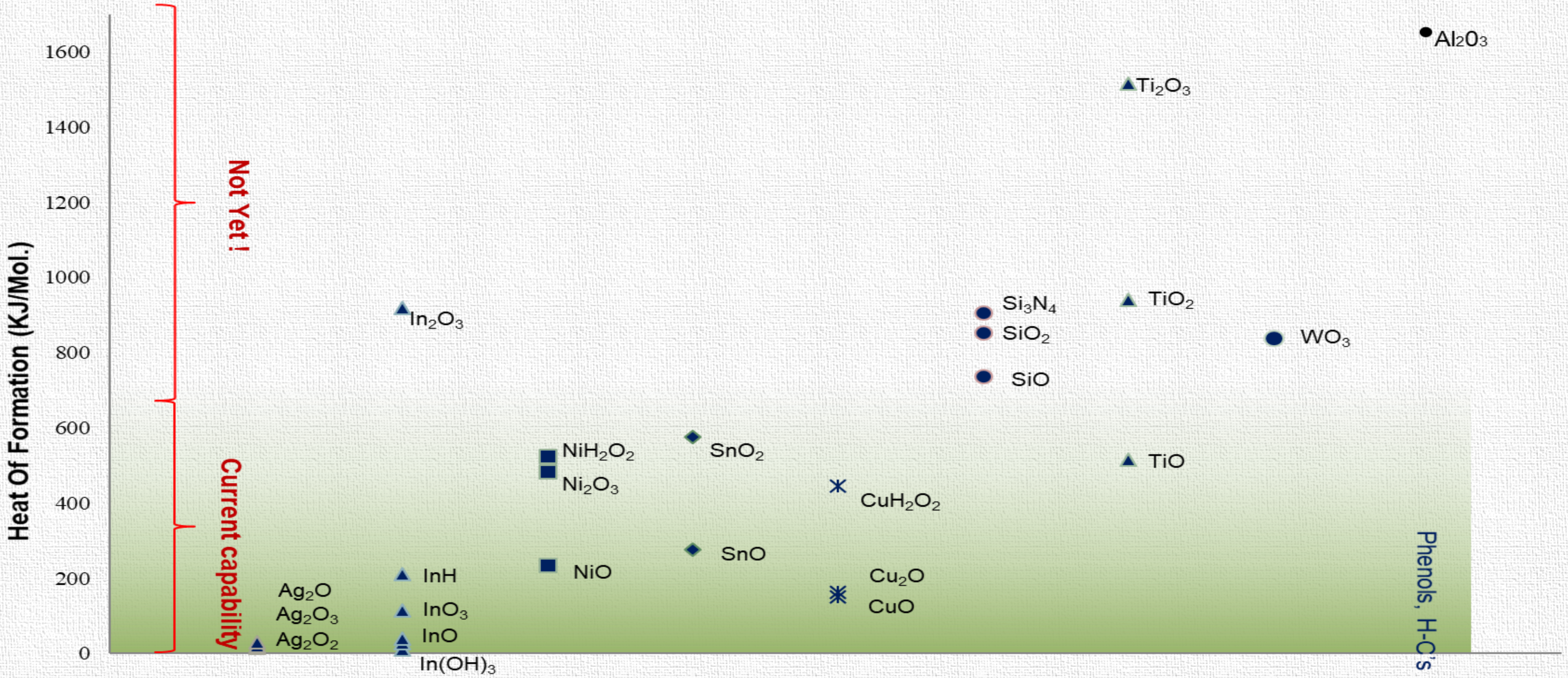
b) Copper treated with He/H_2 only

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

Jump to appendix #1 for examples of Copper Experiment



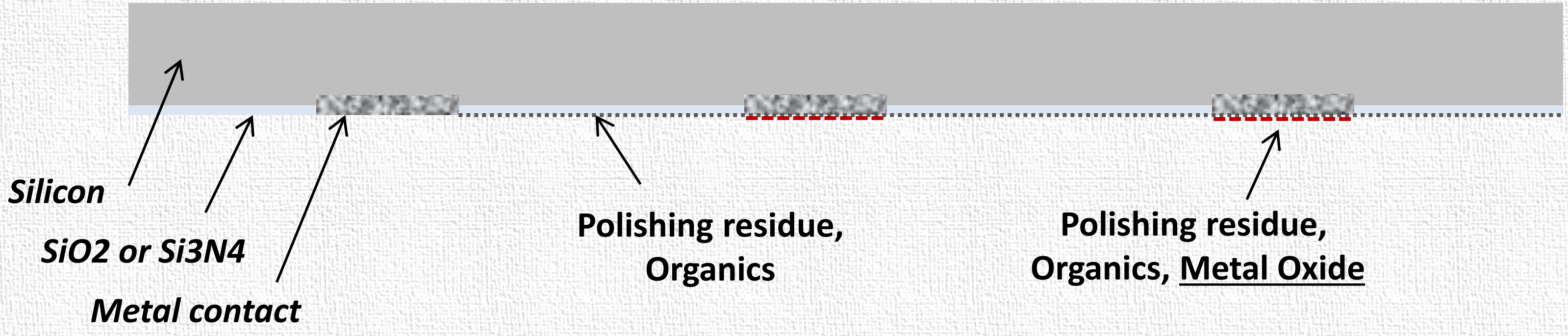
10. Limitations: Not all Oxides are created Equal



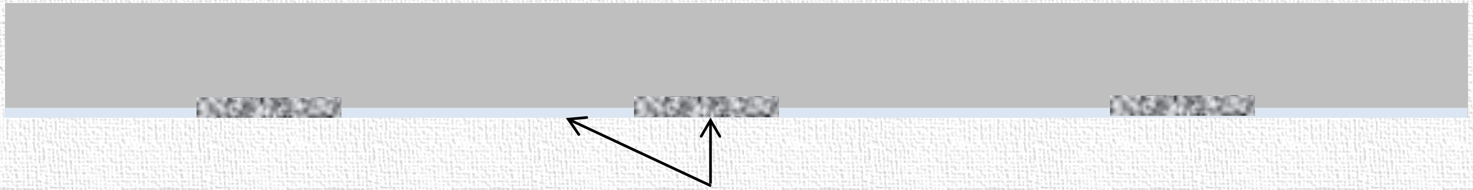
- The thermodynamic "Heat of Formation" (ΔHf) varies widely over the range of metal oxides (from Ag_2O at 30.6 KJ/Mol. To Al_2O_3 at 1 669.8 KJ/Mol.). Our current capability goes up to ~600 KJ/Mol.

Ontos surface preparation for a W2W or D2W bonding process:

- **Staged Parts - Surface Condition:**



- **After Ontos Prep with reducing + passivating dry chemistry:**



Pristine surfaces

Dielectric and metal cleaned, and passivated with monolayer of Nitrogen

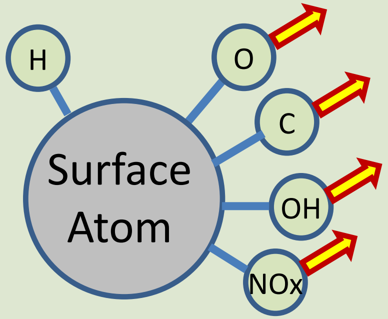
Ideal for direct bond of dielectric and ohmic contacts

11. Surface Activation

Activated surfaces are more receptive to subsequent surface processes

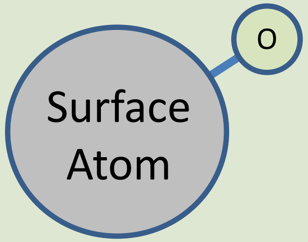
- Different types of Activated Surfaces can be achieved with Ontos:

Hydrogen-Terminated



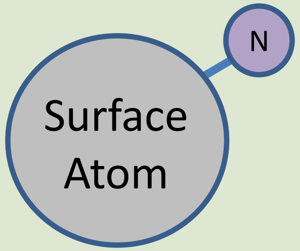
- H* radicals volatilize surface contaminants.
- Leaves surface bonds Hydrogen terminated.
- Highly activated surface.
- Ready for engineered termination.

Oxygen-Terminated



- Dense O* available for:
- Photoresist descum.
- Photoresist adhesion.
- Dielectric adhesion.
- Dielectric wetting.
- Passivation.
- AR coating adhesion.
- Oxide direct Bonding.

Nitrogen-Terminated



- Epi Growth, ALD
- Thin film deposition, metals dielectrics, SC.
- Adhesive Assembly
- Passivation
- Direct Bonding (SC, Si_3N_4)
- Wire, Bump Bonding
- Wet etch metals

11. Surface Activation (Capillary Underfill)

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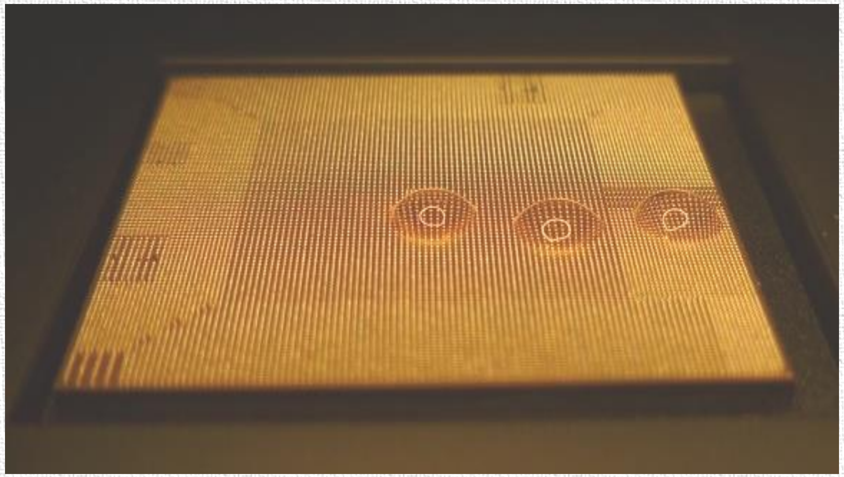
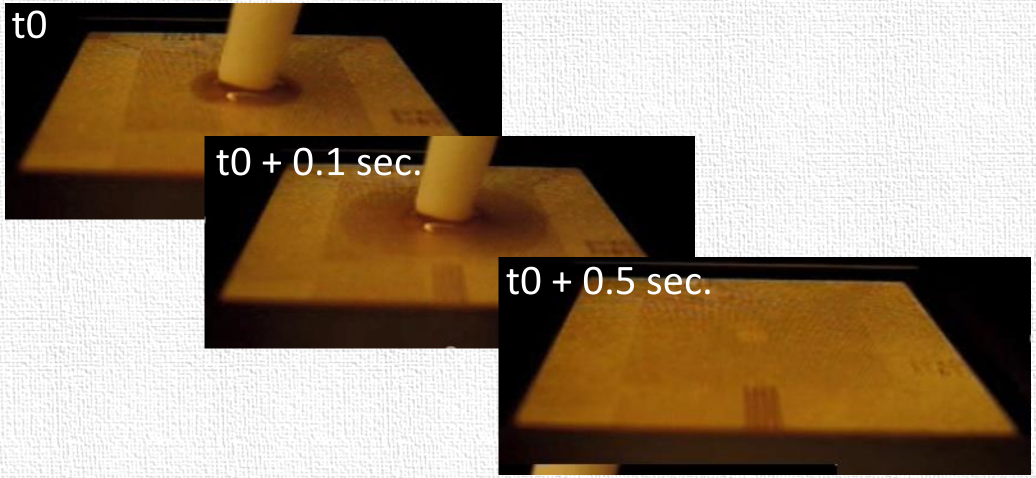
Example: High-density Bumps (SnAg) on BGA chip (Si_3N_4 Passivation)



Untreated

- No wetting of the bumps or Si_3N_4 passivation

- **Poor wicking and adhesion of underfill**



After treatment with Ontos:

- Using reducing chemistry for bump de-oxidation of chip and substrate before flip chip.
- Superb wetting of both bumps and passivation.

- **Excellent wicking and adhesion of underfill in flip chip gap.**

11. Surface Activation (encapsulation perimeter)

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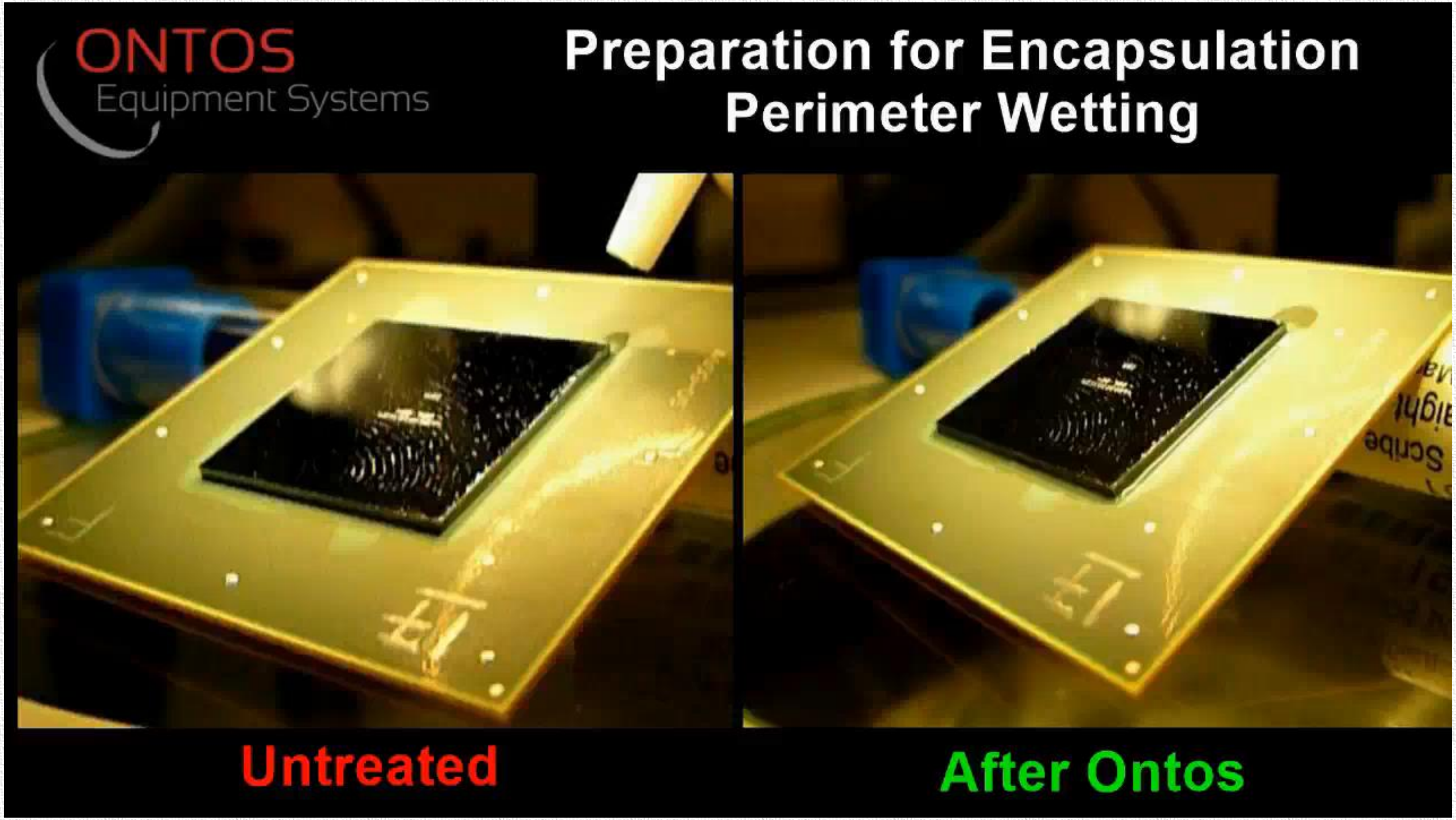
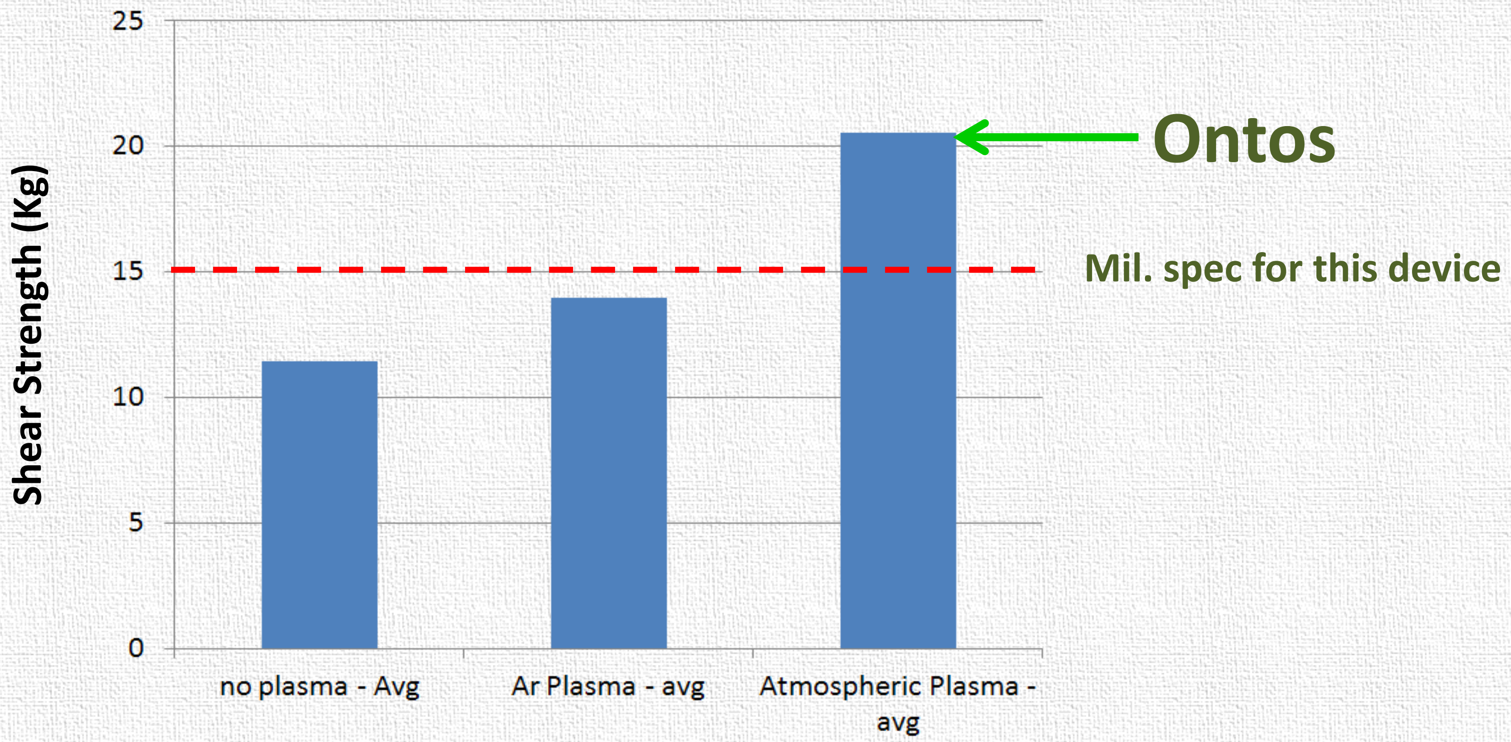


11. Surface Activation (Die Attach Adhesion)

Ontos reducing chemistry creates clean, activated surfaces for adhesive bonding:

Example: Epoxy adhesion of Si chip to Al_2O_3 substrate.



Ontos nearly **doubles** the shear strength **over no preparation**; and does **50% better than Argon plasma**.

11. Surface Activation (Direct Bonding)

Pdf: Click for video on line

Ontos chemistry creates clean, activated surfaces for direct bonding: