ONTOS
Equipment Systems

Surface Modification and Activation with Atmospheric Plasma

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INTRODUCTION

- Surfaces exposed to room air environment are typically contaminated with hydrocarbons, oxygen, nitrous compounds, hydroxide, water, and much more.

Atmospheric Plasma

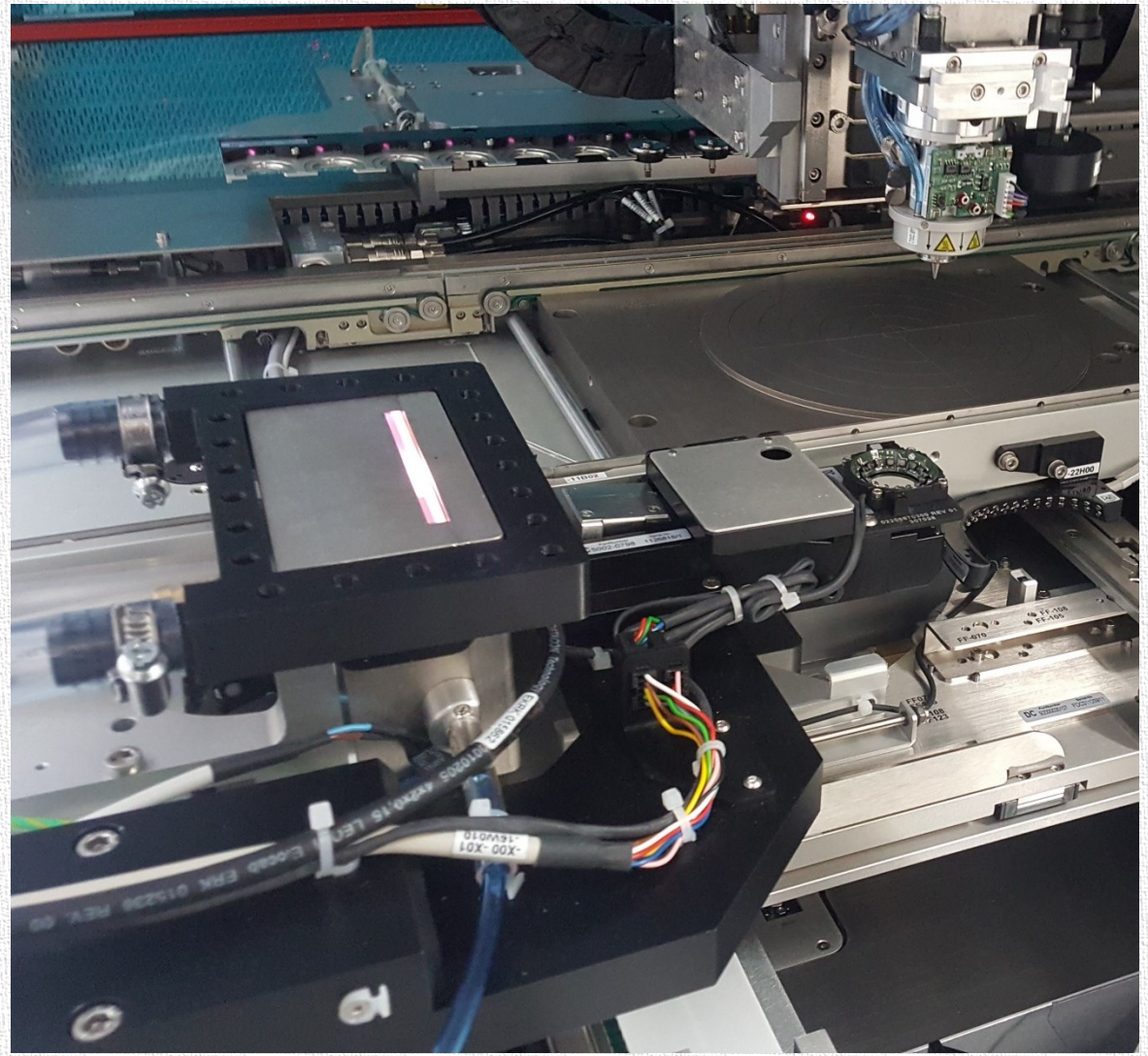
- It is capable of Reducing, Nitridizing, or Oxidizing surfaces without a vacuum chamber.
- It provides treatments that leave surfaces highly activated for subsequent processes such as functionalization, deposition or adhesive processes.
- It is an environmentally friendly alternative to chemical treatment, enabling continuous-feed surface preparation.

Atmospheric Plasma - Semiconductor Applications

- Removal of organic contamination.
- Mask and Nanoimprint Stamp cleaning
- Removal of metal oxide, ohmic interconnect.
- Surface passivation, adjust surface functional groups.
- Surface activation:
  - Adhesive bonding, Adhesive assembly (epoxies, silicones, etc.)
  - Metal-Metal bonding, Hybrid chip interconnects (Au, Pt, Cu, Sn…)
  - Direct bonding, Solder-less, Adhesive-less assembly (fusion bonding).
  - Surface wetting, Capillary wicking enhancement.
- Preparation for plating.

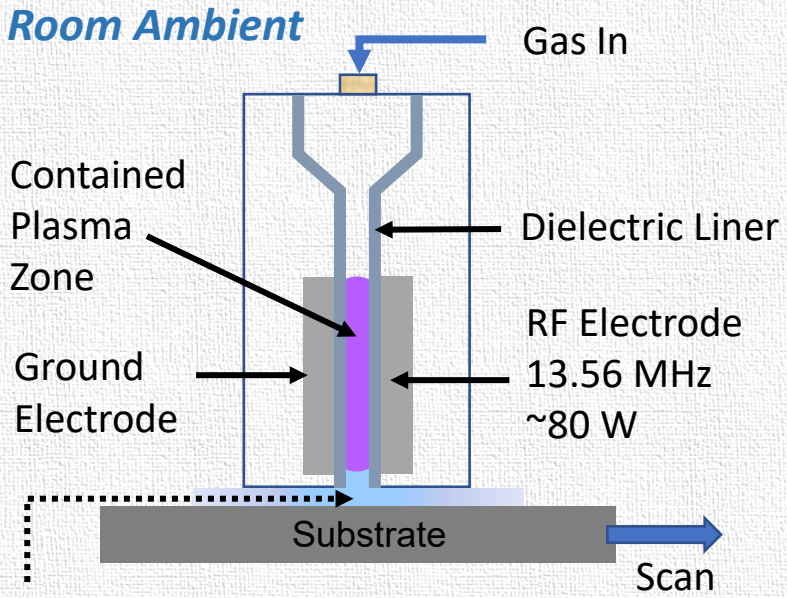
Atmospheric Plasma Benefits

- Plasma Processing without vacuum
  - Fast process with continuous throughput.
  - Can be integrated in line or in processing tools
- Treat surfaces with gas-phase radicals
  - Oxidizing chemistry
  - Reducing chemistry
  - Nitridizing chemistry
- Ideal for sensitive surfaces:
  - Low temperature < 100 °C
  - No bombardment



ONTOS ATMOSPHERIC PLASMA PRINCIPLE

Cross Section of the Plasma Head



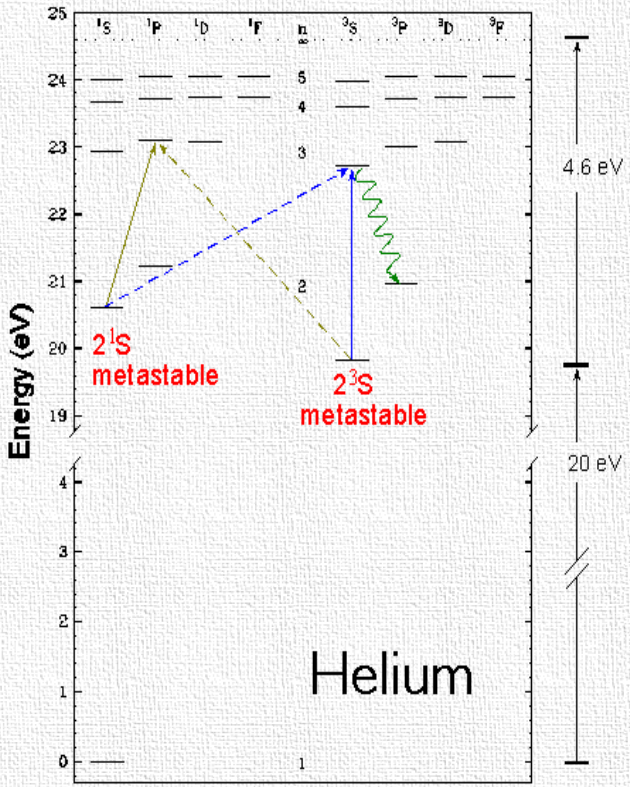
Downstream active radicals

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

- Highly-energetic species of the plasma (ions, hot electrons) have short lifetimes at atmospheric pressure, they are re-combined within a few microns of exiting the plasma zone. They are confined within the plasma head
- 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.
- The flow of downstream gas from the atmospheric plasma head sweeps 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.

Why Using Helium as a Carrier Gas ?

- 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 it occurs strongly when the Metastable Helium Atoms **contact the substrate surface**.
- It transfers quantum energy to the surface atoms and provides **extra activation energy** for surface chemical reactions.

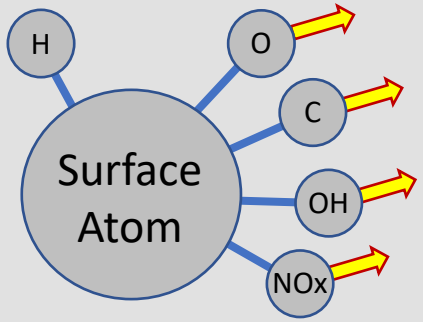


Quantum Energetics Activate Surface Reactions

Surface Chemical Reactions

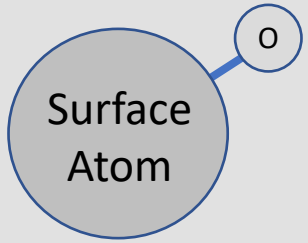
Atmospheric Plasma Provides Activated Chemical Radicals for Surface Preparation for a Variety of Semiconductor Applications

Reducing Chemistry with Hydrogen Radicals



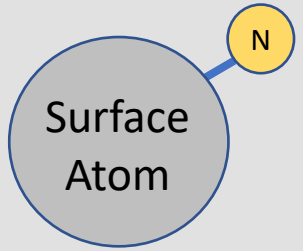
- H* radicals volatilize surface contaminants.
- Leaves surface bonds Hydrogen terminated.
- Highly activated surface.
- Ready for engineered termination.

Oxidizing Chemistry with Oxygen Radicals



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

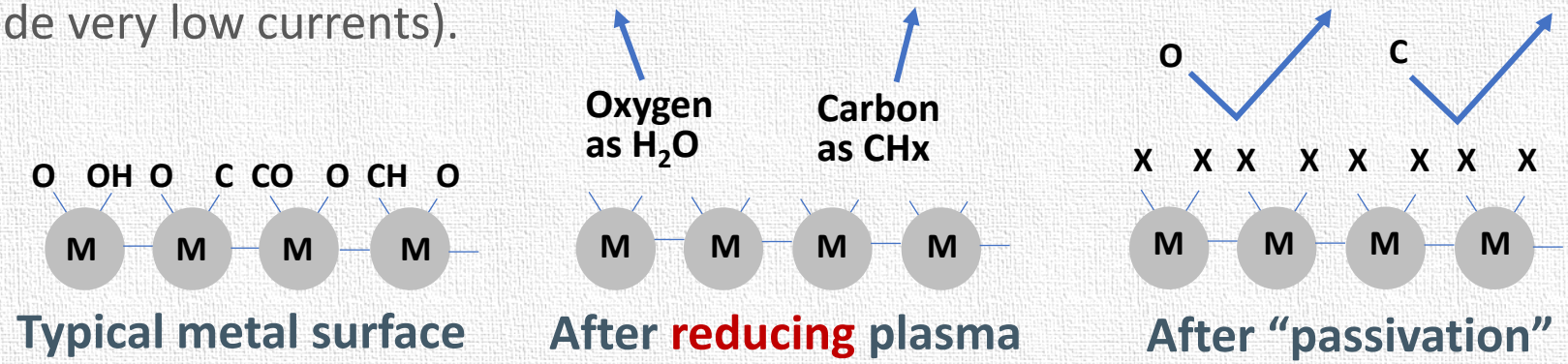
Nitridation Chemistry with Nitrogen radicals



- Epi Growth
- Adhesive Assembly
- Passivation
- Bump Bonding
- Wire Bonding
- Wet Etch of Metals
- Direct S/C Bonding
- Nitride Direct Bonding

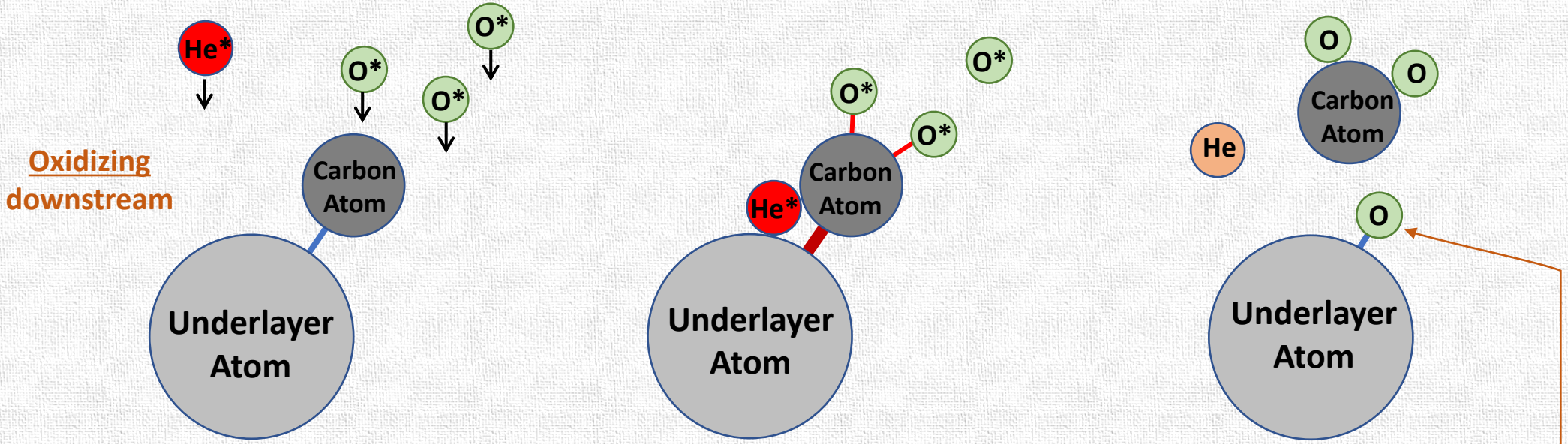
Organic Removal : Oxidizing Or Reducing Chemistry ?

- Ontos Atmospheric Plasma is suited to give the choice of Oxygen-based or Hydrogen-based chemistry.
- When oxidation of the underlying substrate is not a concern, Oxygen chemistry 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).



Organic Removal (Oxidizing Chemistry)

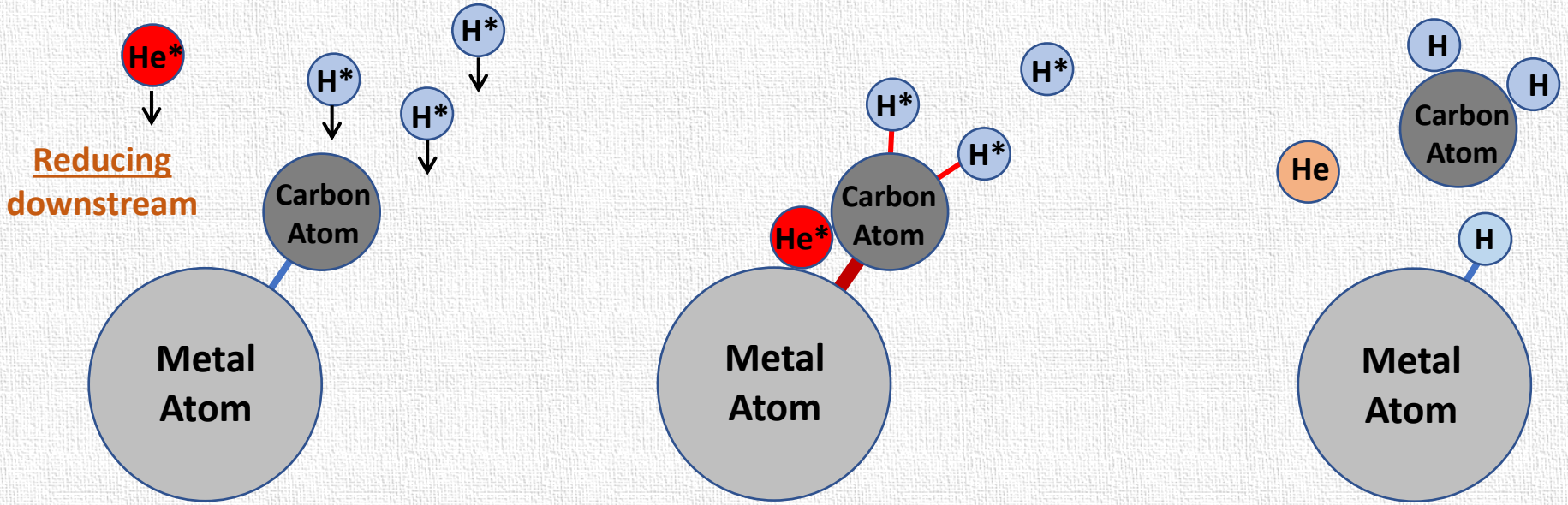
- Oxygen radicals (O*) are highly reactive species ready to react with substrate surface to remove the organic contamination.
- The metastable Helium atoms provide quantum energy directly to the substrate surface. There is essentially no kinetic energy transfer occurring, and therefore, no kinetic damage to the substrate.



The underlayer atom dangling bond is now terminated with Oxygen!
Possibly a method to control oxidation stoichiometry: *Passivation!*

Organic Removal (Reducing Chemistry)

- Hydrogen radicals (H*) are highly reactive species ready to react with substrate surface to remove the organic contamination.
- Reducing reactions are used to remove carbon, Hydroxyl (OH), and other contaminants from the substrate surface.



- Reducing chemistry leaves surface bonds Hydrogen terminated, unless Nitrogen is added to the gas mixture.

Oxygen Descum with Atmospheric Plasma

- The Ontos Chemistry produces a high density of Oxygen radicals – up to ~ $5^{18}/cm^3$.
- At high power and low scan speed, entire films of photoresist, can be removed, even at room temperature.
- Substrate heating increases removal rate.

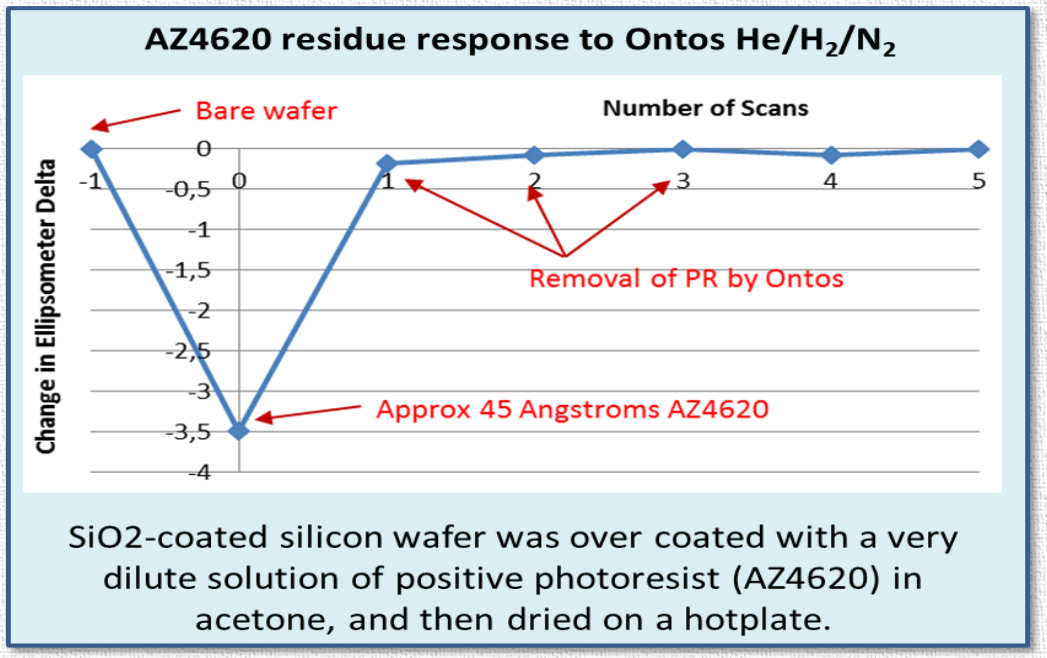
300 nm of i-line photoresist removed (RT, Ontos Oxidizing Chemistry)

- 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 the Photo-Resist Linewidths.
- Process time to descum a 200 mm wafer is approximately 3 minutes.
- It is an excellent process to use when oxidation of exposed surface is not an issue.

80 nm of amorphous carbon removed at room temperature (Ontos Oxygen Chemistry)

Hydrogen Descum with Ontos AP

- In cases where oxidation of exposed metal is not desirable, Hydrogen Chemistry can be used to remove Photoresist residues… and de-oxidize the metal.
- Nitrogen can be added to the Ontos gas mix to passivate the exposed metal against re-oxidation while awaiting deposition.
- Process time to descum a 200mm wafer is approximately 6 minutes.

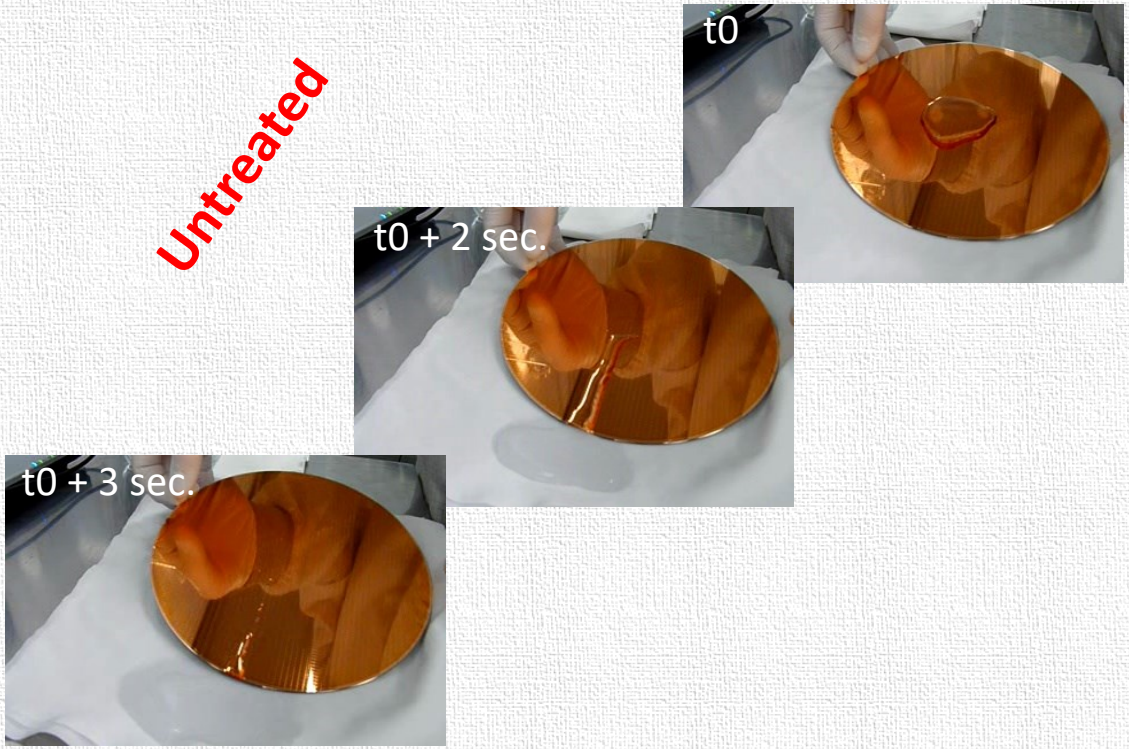


Preparation for Plating (Descum and De-oxidation)

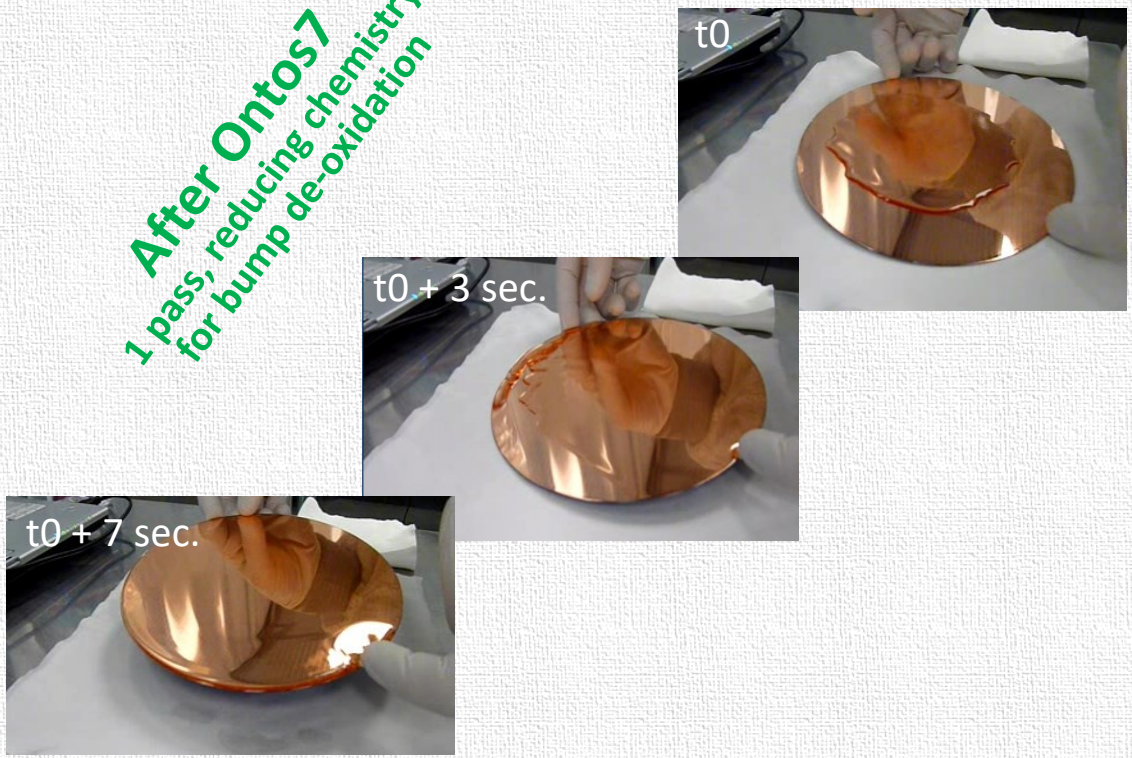
Pdf: Click for video on line

Positive PR over Cu plating base

Untreated



After Ontos7
1 pass, reducing chemistry
for bump de-oxidation



No wetting of Photoresist or metal pattern

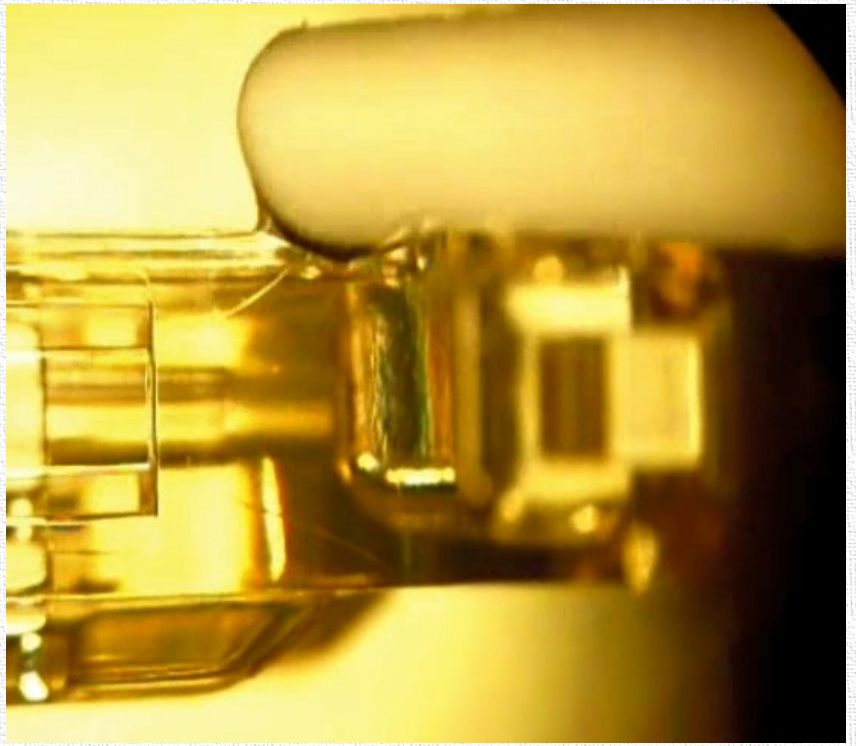
- Process voids
- Non-uniformity
- Time control issues

Superb wetting of both Photoresist and Metal

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

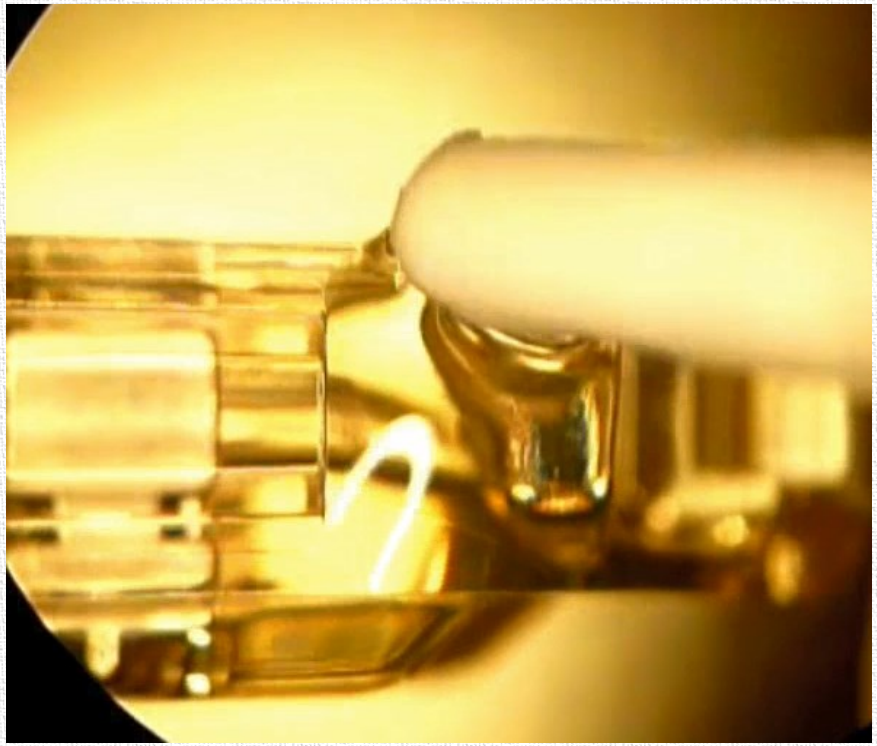
Pacemaker module: Wetting on Tecothane

Untreated



No wetting

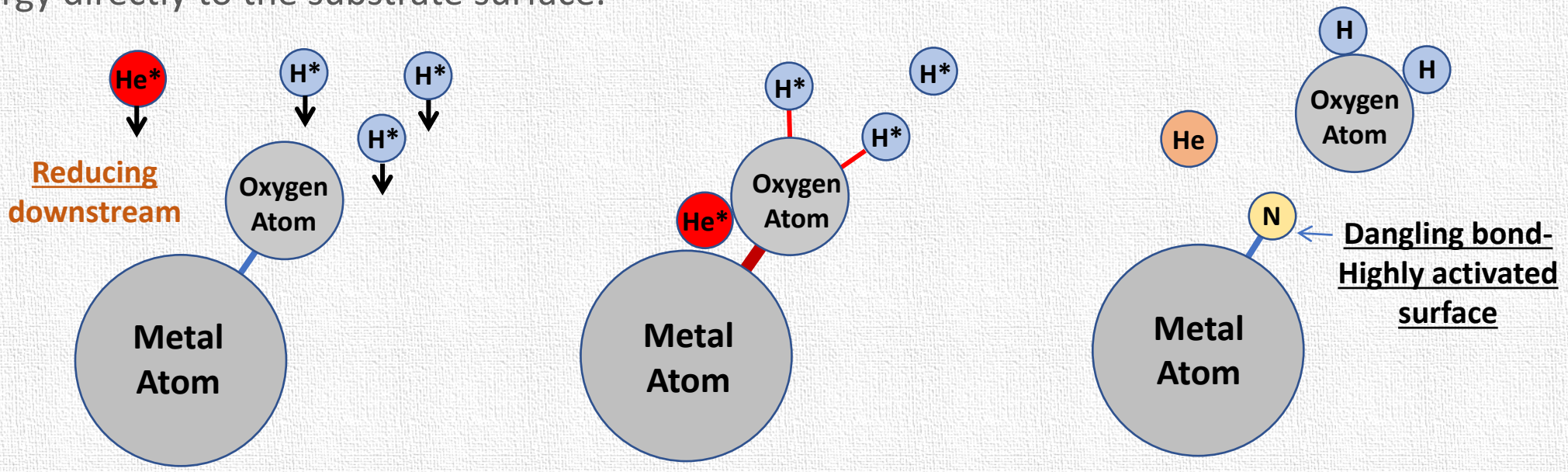
After Ontos7
(Single Pass, Oxidizing chemistry)



Improved wetting

Oxide Removal (direct bonding, hybrid interconnect)

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



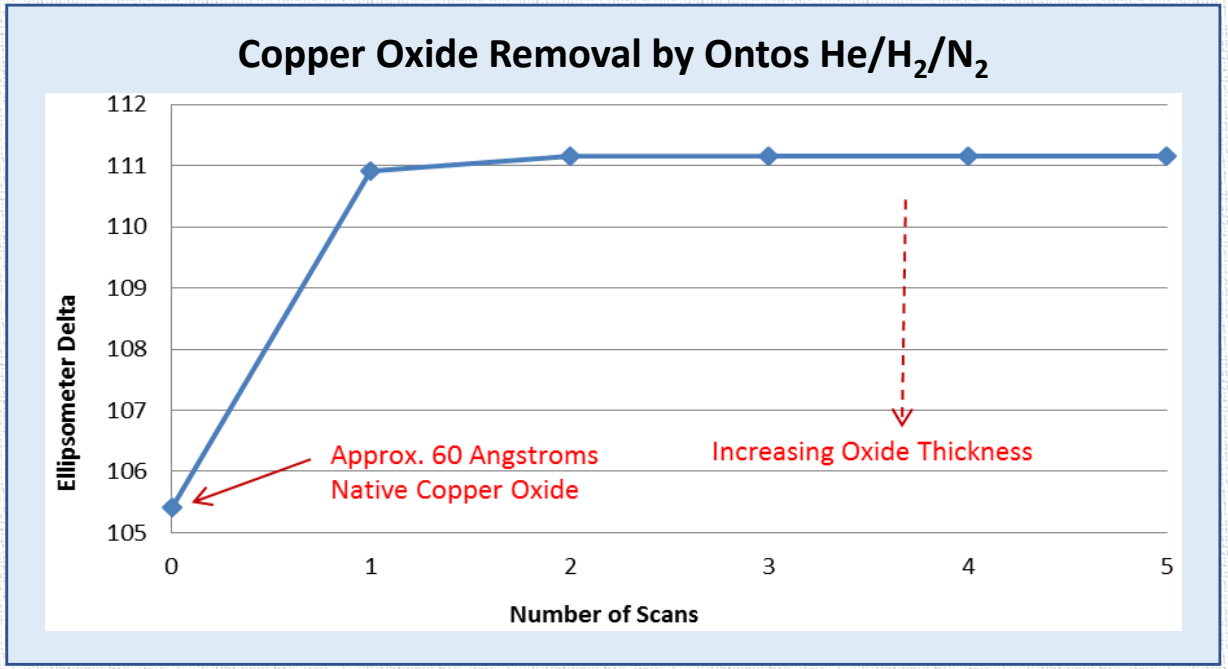
- Reducing Chemistry removes organic contamination **and** metal oxides.
- Additional species can be added to the surface to protect dangling bonds for long periods (hours to days) to inhibit surface re-contamination.

Oxide can be reduced from In, Sn, Ni, Cu, Sb, Ag, Au, and more.
Typical passivation lasts for 20+ hours on Copper at Room temperature

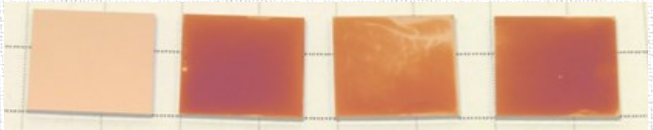
Oxide Removal (direct bonding, hybrid interconnect)

Oxygen Removal from Copper Surface

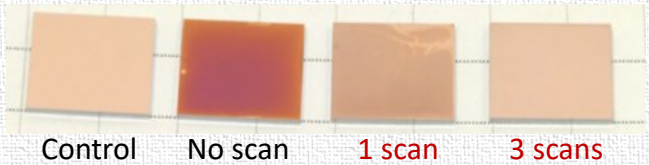
- Exposed to atmosphere, Copper growths at room temperature a surface layer of Cupric Oxide (CuO).
- Atmospheric Plasma with reducing chemistry (Hydrogen-based excited species) is used to remove oxidation from the surface.



4 Cu/Si coupons out of the box



3 coupons hotplate oxidized – 150°C, 12 minutes
(Approximately 400 Angstroms)



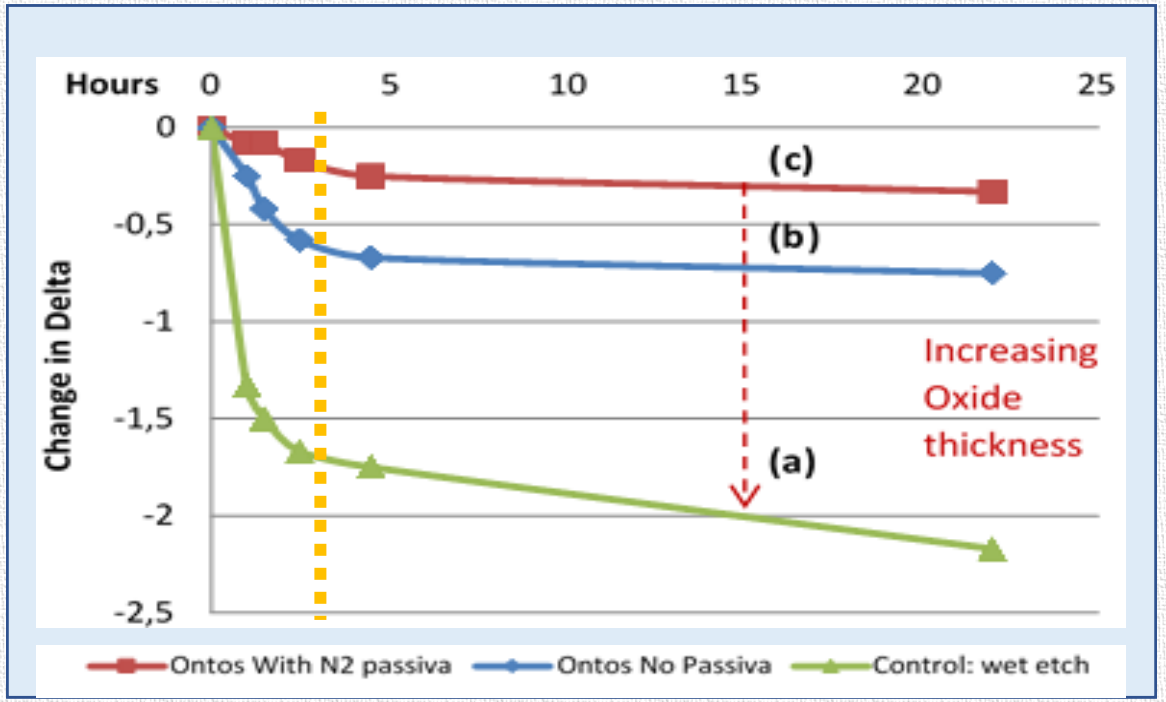
Atmospheric Plasma reduces Cu Oxide at Rom Temperature.
3 scans returns Cu to native state.

PASSIVATION (DIRECT BONDING, HYBRID INTERCONNECT)

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 $He/H_2/N_2$

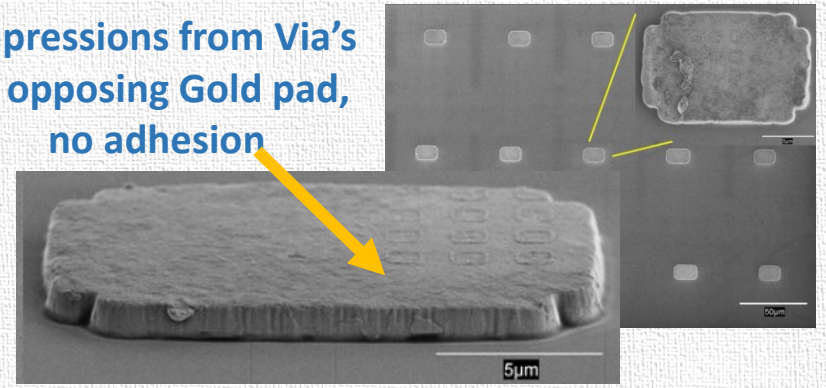
Hybrid Chip Interconnect

Atmospheric Plasma produces a pristine, activated surface for:

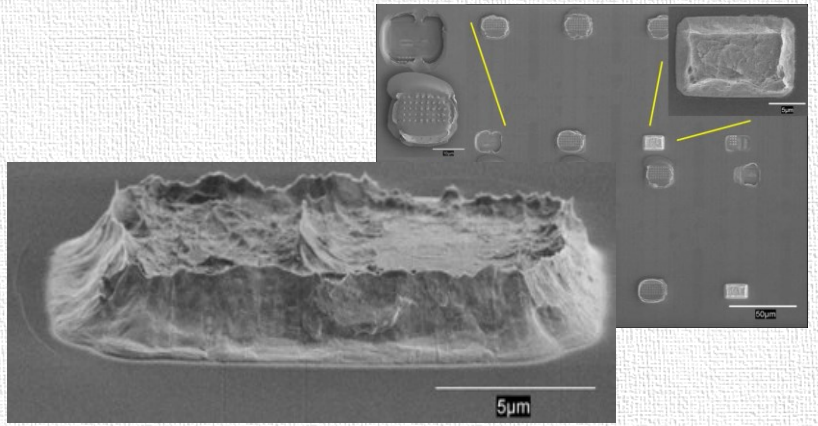
- **Direct Bonding:**
  - Semiconductor-to-semiconductor (at RT)
  - Oxide-to-Oxide (at RT)
  - Oxide-to-Nitride (at RT)
  - Oxide-to-semiconductor (at RT)
- **Metal-to-metal:**
  - Au – Au (As low as 100°C)
  - In – In (at RT)
  - In – metal pad (at RT)
  - In – Ag (at RT)
  - SnAg – Cu (at 175°C)
  - SAC – Cu (at 175°C)
  - SAC – SAC (at 175°C)
  - … more

Gold-to-Gold Direct Bonding

- Low-Temp. Au-Au Thermocompression Flip Chip Bonding (necessitated by chip temperature restrictions to 200°C)
- After 200°C thermo-compression bonding and pull test, Untreated Gold Pads show adequate compression, but very poor adhesion.



- Bonded under identical bonding conditions, with Ontos atmospheric plasma surface preparation process
- Yields remarkable Gold-to-Gold adhesion. Pull-apart tests showed metallurgical tensile rupture within the Gold bulk, and adhesion was so good that many Gold bond pads were ripped away from the substrate, taking chunks of underlying Silicon with them.



- We have determined the following Temperatures for successful Au-Au bonding after Ontos treatment:
  - Sputtered or evaporated Au: As low as 100°C
  - Electroplated Au: As low as 125°C
  - Electroless Au: As low as 150°C

Conclusion

- Atmospheric Plasma provides a rapid and effective surface treatment which enhances subsequent bonding or plating processes. No vacuum system is required, thus enabling continuous throughput.

- With a single surface treatment process, it achieves:

  1) Organics Removal.
  2) Reduction of oxidation on the exposed metal surfaces.
  3) Passivation of the metal surfaces to inhibit oxide regrowth
  4) Activation of the surfaces to provide thorough wetting

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THANK YOU FOR YOUR ATTENTION

SURFACE MODIFICATION AND ACTIVATION WITH ATMOSPHERIC PLASMA

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