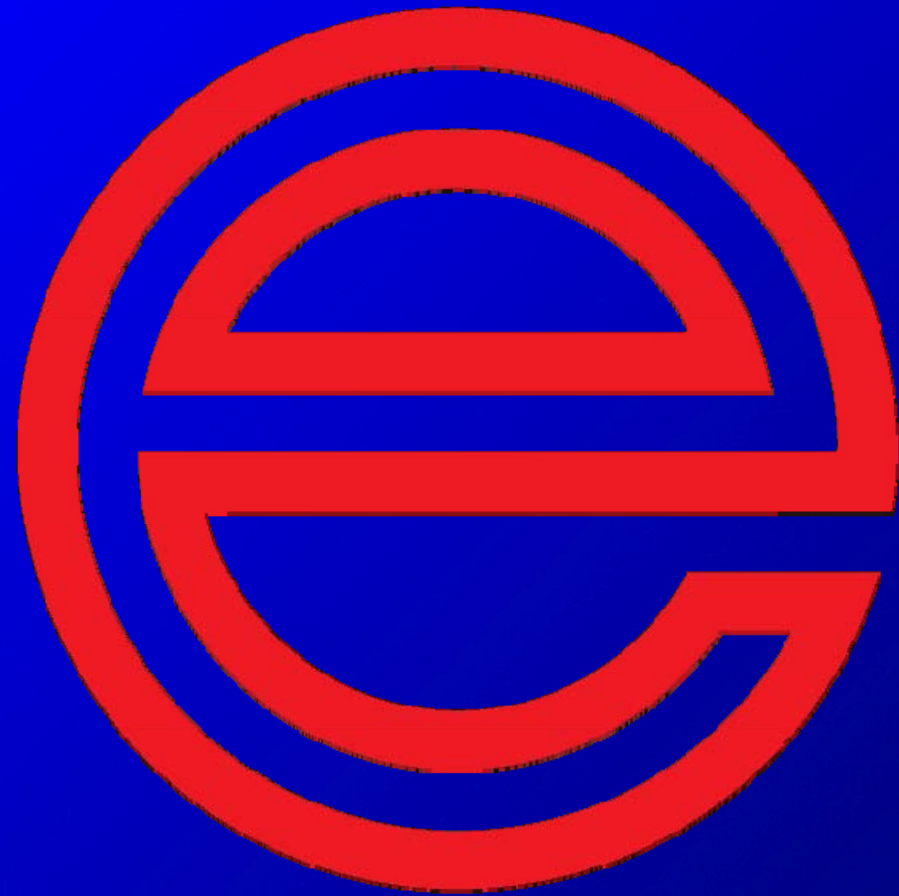



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Reducing Solar Module  
Cost with Atmospheric  
Plasma Surface  
Modification

A "Green" Technology

Presented by

Rory A. Wolf, V.P.  
Enercon Industries Corporation

# Presentation Outline

- Plasma Surface Modification
- Plasmas for Fabricating PV Cells
- PV Cell Fabrication Trend
- Atmospheric (Dry) Plasma Surface (APT) Modification Effects
- PV Cell Surface Preparation & Cleaning
- APT Prescriptions for PV Materials
- Conclusions

# Plasma Surface Modification

- **Plasma surface modification technology in PV cell manufacturing:**
  - Deposition of amorphous SiN layers
  - Utilize vacuum PECVD process
- **Create anti-reflection and surface passivation on thin-film solar cells**
- **Vacuum plasma etching in barrel-type reactors for edge isolation**

# Plasma Surface Modification

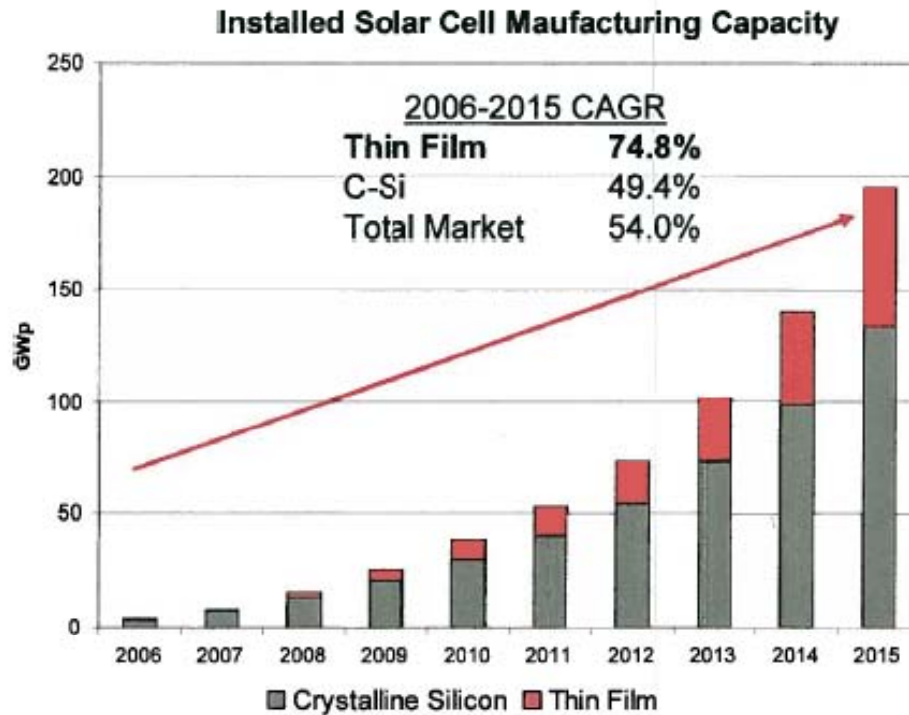
- **Increasing chemical waste disposal issues**
- **New interest in plasma systems**
  - **dry etching**
  - **surface cleaning**
  - **adhesion promotion**
- **Warrants fresh investigation of efficiencies**

# Plasmas for Fabricating PV Cells

- Use of plasmas dependent upon PV materials and cycle time
- Vacuum plasmas not a bridge to high volume continuous process
- SiNx deposition typically batch processes
- Can work in semi-continuous mode by exchanging materials after treatment and return to one atmosphere
- Not economical for high throughput etching, cleaning and functionalizing

# PV Cell Fabrication Trends

## Thin Film is Fastest Growing PV Technology



### Thin Film Drivers

- Cost advantage: Thin Film reduces the amount of light absorbing material, leading to a reduction of CoO while technology increases efficiency
- Shorter energy payback period: Production of thin film modules is less energy intensive
- Temperature coefficient: The performance of modules remain more stable with increasing temperature

Source: Commerzbank and Oerlikon estimates

# PV Cell Fabrication Trends

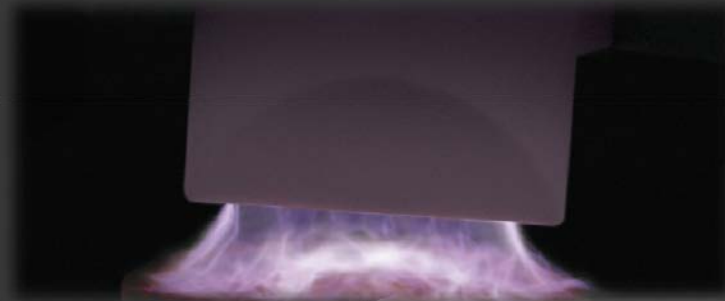
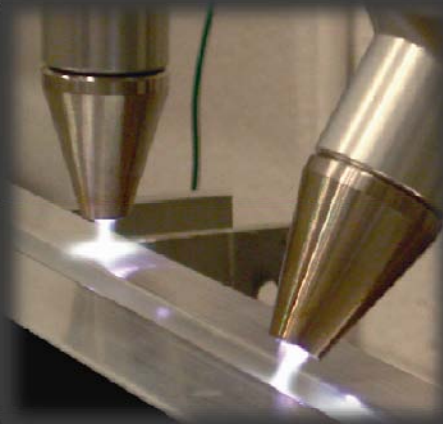
## Organic Thin-Film Solar Cells on Plastic

- Organic semiconductive materials are dissolved in solvents or inks and printed or coated onto a plastic substrate in a continuous roll-to-roll process.
- Less expensive than silicon, cadmium or tellurium
- Prototypes in production now.
  - **Example 1:** clear plastic top layer, a coating of prepolymer adhesive, then ink containing fullerene conductive nano-carbon clusters, and another liquid polymer coating, applied to PET film with an SiO<sub>x</sub> coating.
  - **Example 2:** Use of organic inks for solar cells. The ink lets electrons pass to an electrically conductive polymer layer on a plastic substrate.

# PV Cell Fabrication Trends

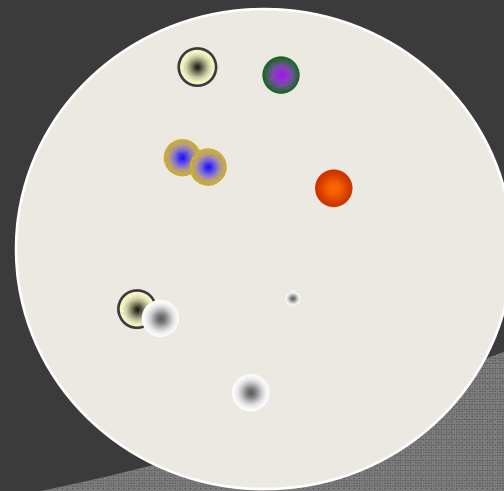
- **Wide range of materials being examined to maximize solar efficiencies.**
- **Opportunity integrate continuous in-line processes for rigid/flexible PV cells**
- **Utilize atmospheric (gas phase) variable chemistry surface modification technology for dissimilar materials to improve fabrication efficiency.**

# Atmospheric Plasma Surface Modification

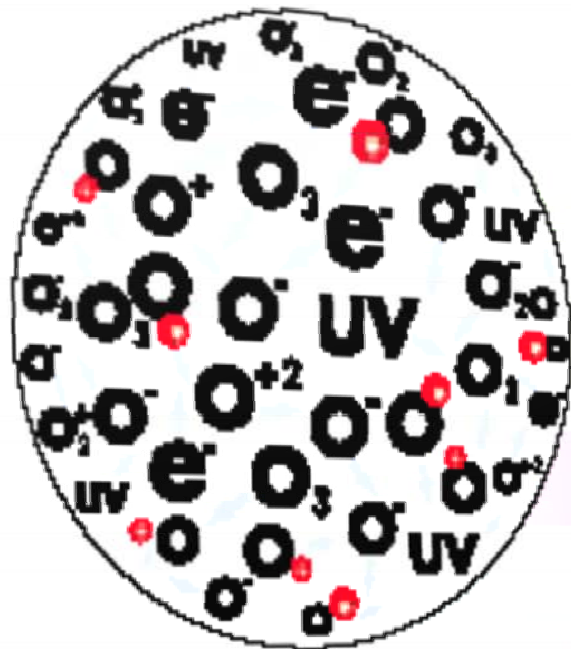


# Atmospheric Plasma Surface Modification

plasma :  $n$  ; “Fourth state of matter”, (Solid, Liquid, Gas, Plasma.) Mixture of charged ions & energetic electrons generally in equilibrium.



# Atmospheric Plasma Surface Modification



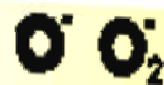
PLASMA



Free Radical (highly reactive)



Ozone



Negative Ions



Ultraviolet Light Photon



Positive Ions

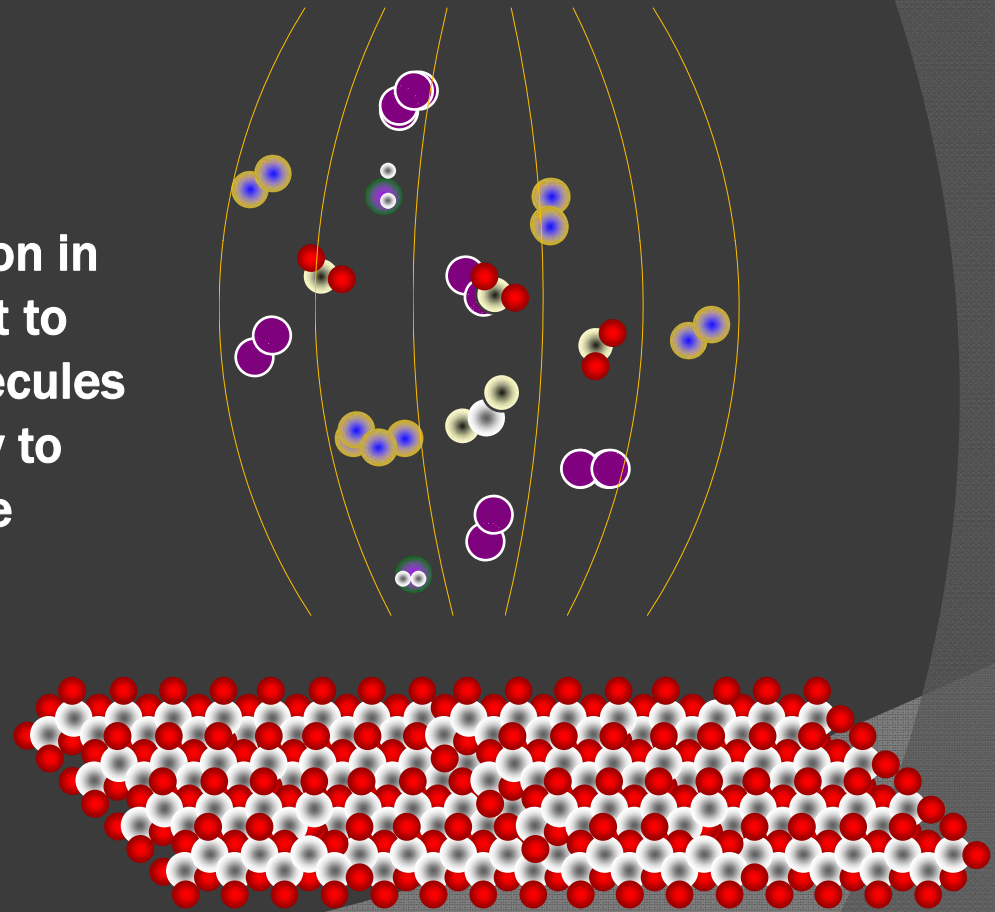


Electron

# Atmospheric Plasma Surface Modification

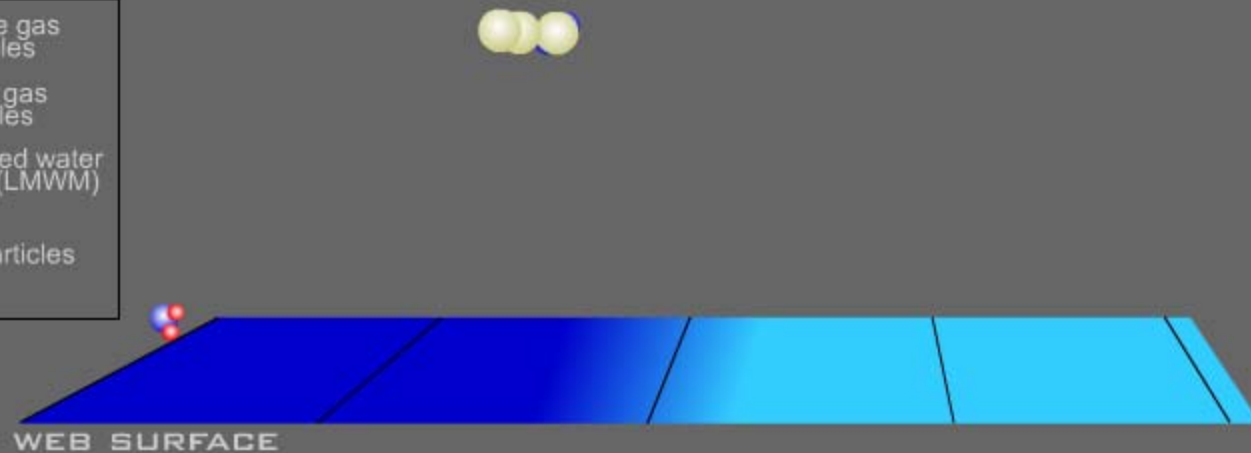
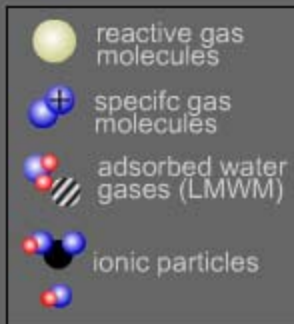
## Recipe

- 1) Take one photon, and allow it to randomly liberate one bound electron from a gas molecule.
- 2) Accelerate this free electron in an electrical field, forcing it to collide with other gas molecules with enough kinetic energy to separate the atoms, or free more electrons.
- 3) Increase power in the electric field to create an avalanche of electron collisions.



# Atmospheric Plasma Surface Modification

## PlasmaTreat<sup>3</sup>™



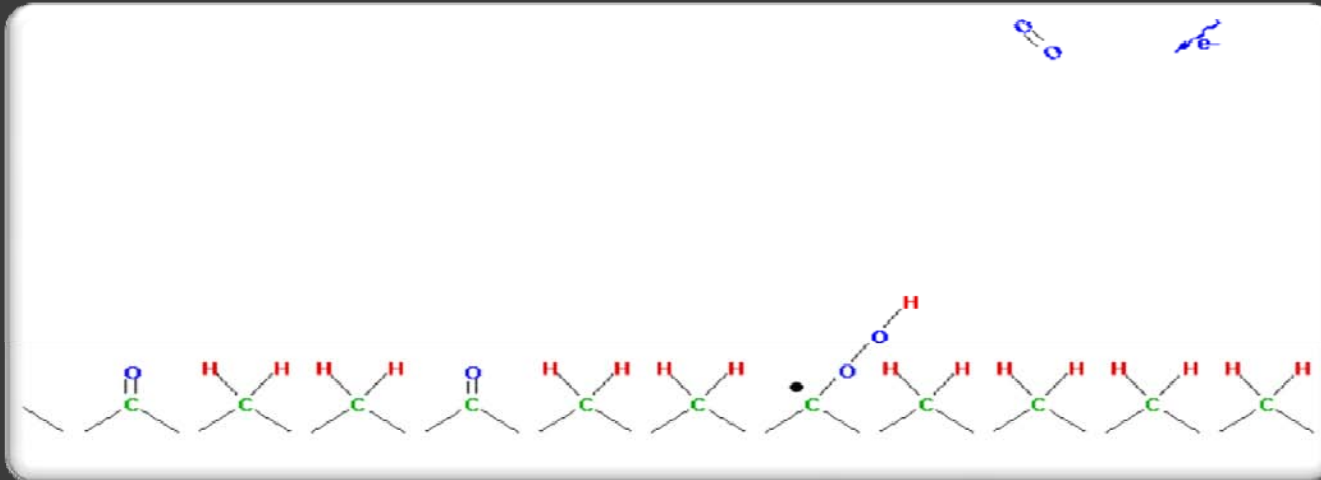
### HOW PLASMA FUNCTIONALIZES A SURFACE -

Reactive gas molecules are accelerated or diffuse towards the target surface under the influence of electric and/or magnetic fields. Low molecular weight materials (LMWM) such as water, adsorbed gases and polymer fragments are knocked off the surface of the film to expose a fresh, clean surface of the bulk substrate. At the same time a percentage of the reactive components of the plasma gas mixture with sufficient energy to bond to the freshly exposed bulk substrate, do so thus changing the chemistry of the substrate surface to impart the desired functionality.

# Atmospheric Plasma Surface Modification

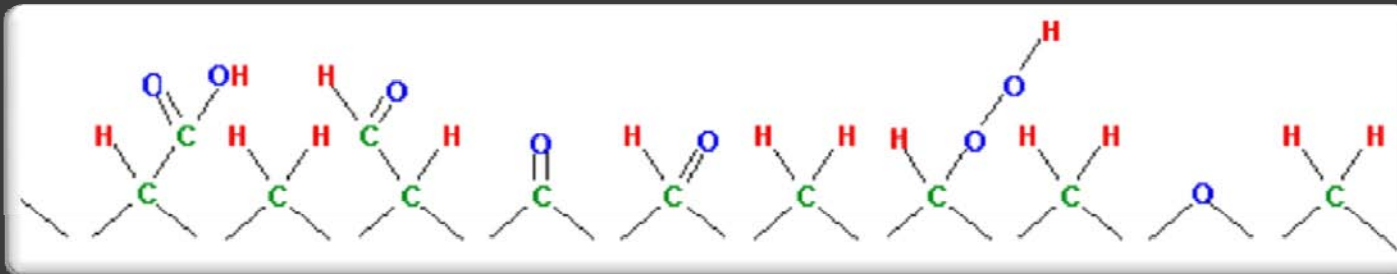
- **Plasma Activation** ⇒ Changes free radicals on the surface by substituting chemical groups on the polymer chain being modified.
- **Plasma Deposition** ⇒ Hydroxyl, carbonyl, carboxyl, carboxylic, amino-carboxyl, and amine chemical groups on surface
- **Plasma-Induced Grafting** ⇒ Free radicals are created along the polymer backbone.

# Atmospheric Plasma Surface Modification



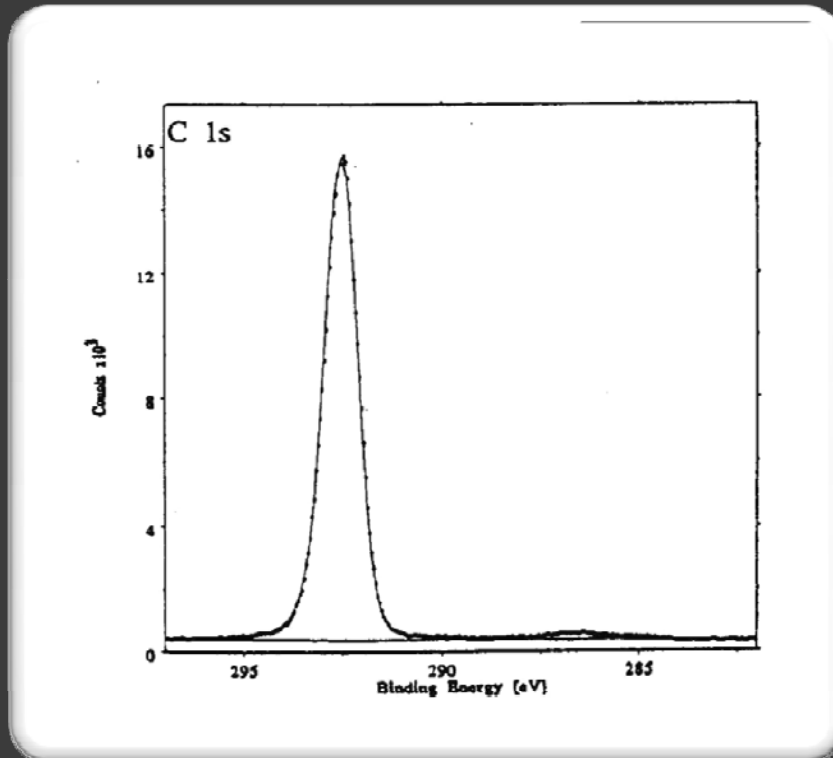
- Animation demonstrates only one of the possible reaction pathways during plasma-chemical oxidation of polyolefins.
- Reaction initiated with atomic oxygen, which abstracts an hydrogen atom from the surface.
- Results in a free radical on the surface, which can react with an oxygen molecule to produce a hydroperoxide group, which can decay into a keton group.

# Atmospheric Plasma Surface Modification

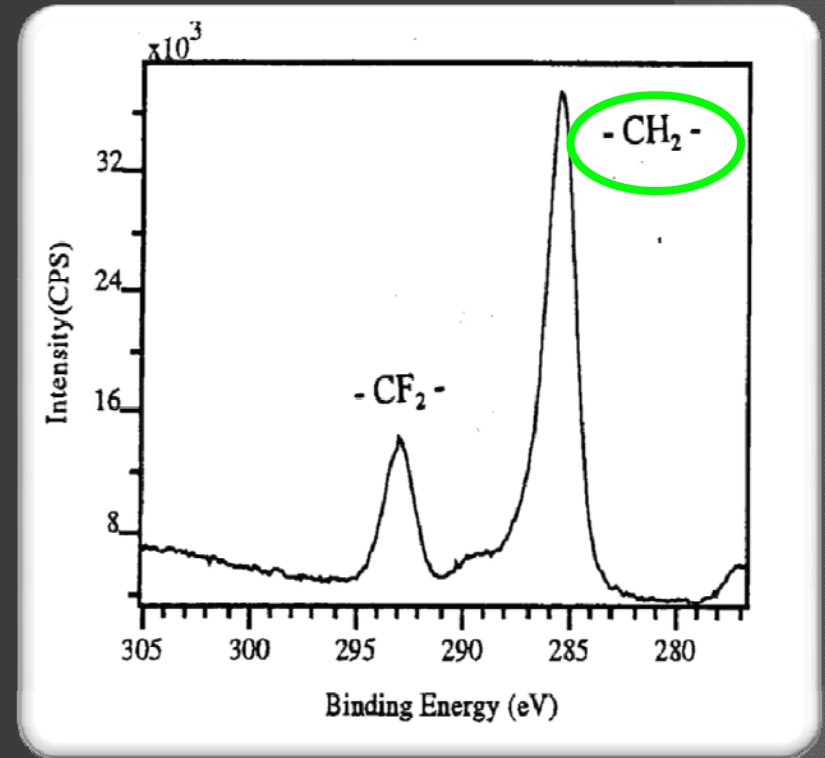


- Besides keton groups, also formed aldehyd, carboxyl, hydroperoxide, hydroxide, and ester groups (above).
- Plasma oxidation results in breaking the polymer chains and material removal (ablation)
- Specific surface functionalization possible under precise control of the reaction conditions.

# Atmospheric Plasma Surface Modification



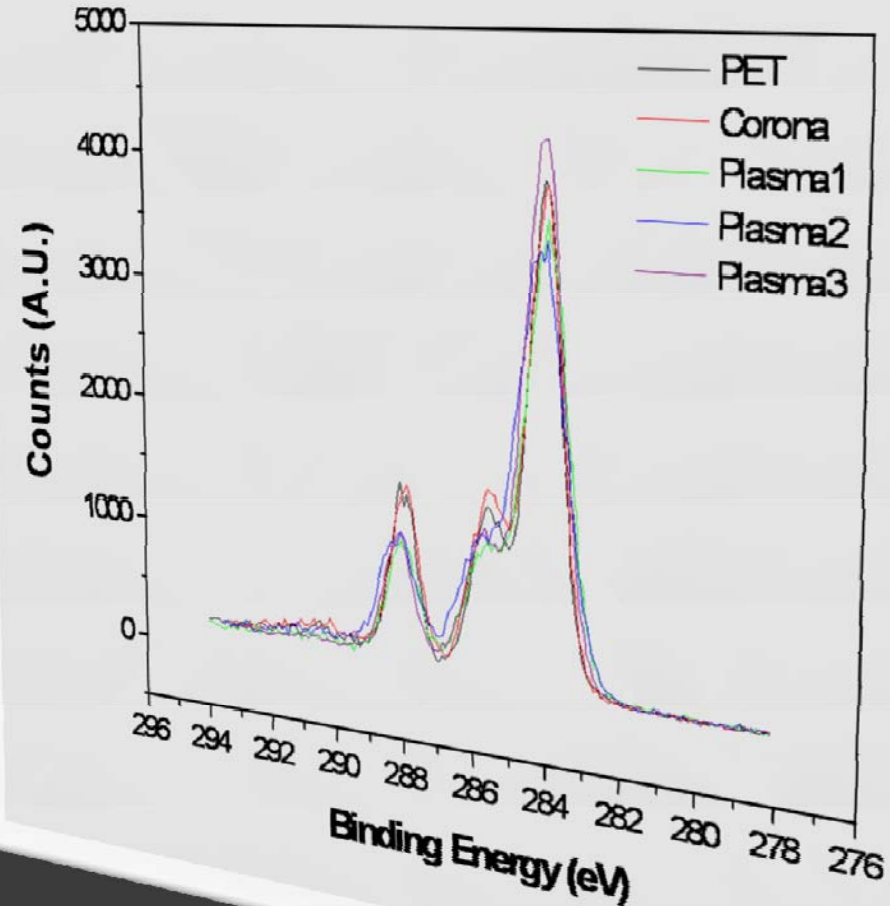
XPS spectrum results of untreated PTFE sample



XPS spectrum results of treated PTFE sample

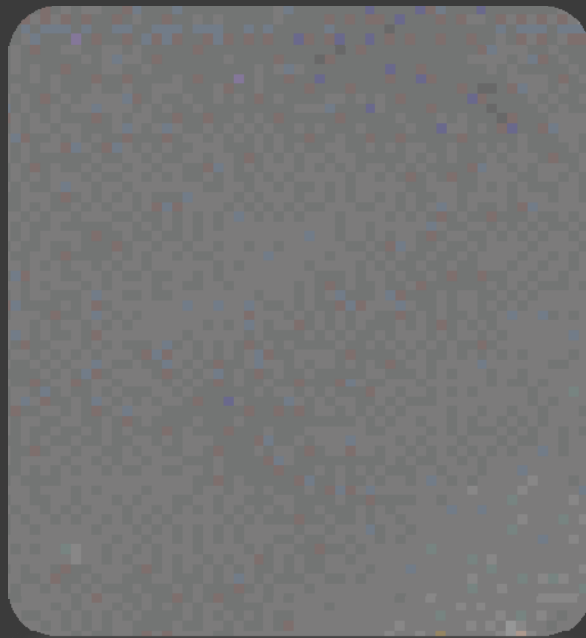
# Atmospheric Plasma Surface Modification

Peak Broadening occurs due to multiple functional groups being present on the surface.



# Atmospheric Plasma Surface Modification

Plasma Treatment Micro-Etching Effect  
Polyethylene (30,000 SEM magnification)



Original Polymer



Plasma-Treated

# Roll-to-Roll PV Surface Cleaning Prior to Si Deposition

## Base Materials

- Lightweight, Flexible
- Will not shatter or be damaged during manufacture, handling, and subsequent operation in the field
- Thin stainless steel substrates, for example, have thermal time constant  $<10$  ms - can be quickly heated and cooled to eliminate waiting for temperature stabilization
- Typically carry rolling oil deposits which must be removed
- Transport in deposition chambers is simple and reliable with little component wear, resulting in very low machine maintenance costs.

## Polymer Encapsulation Materials

- Polymers such as EVA and Tefzel are flexible and lightweight
- Contaminated with residual organic polymer fragments, water, adsorbed gases

# Roll-to-Roll PV Surface Cleaning Prior to Si Deposition

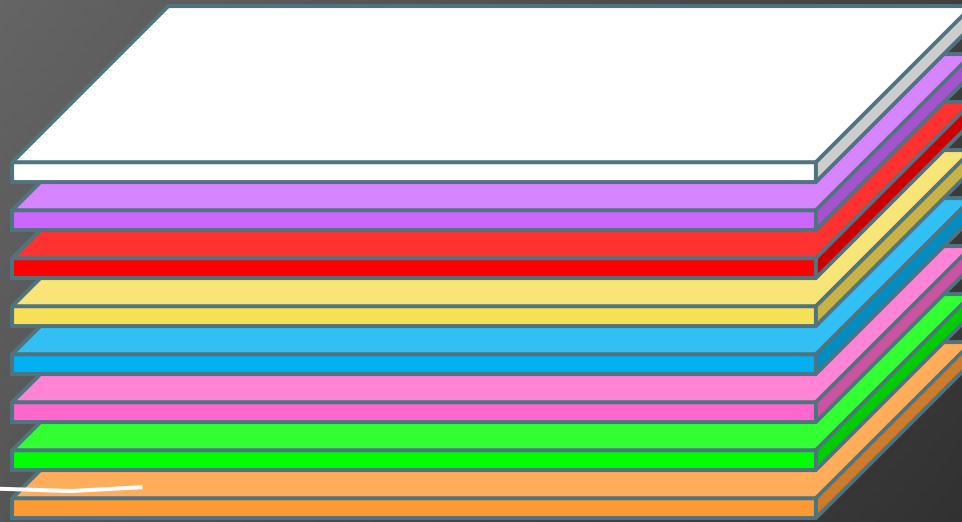
## Existing Base Material Wet Cleaning

- Roll material washed to produce clean, dry, particle-free substrate material suitable for Si deposition
- Web transported through detergent cleaning station, de-ionized water rinsing, IR drying

## Advantages of APT Cleaning/Functionalizing of Base, Encapsulation Films

- Base material contaminates volatilized/vaporized, increasing cleaning process efficiency.
- Encapsulant functionalization increases surface-to-reactive adhesive and surface-to-primer bond strength to flexible structures, and glass.

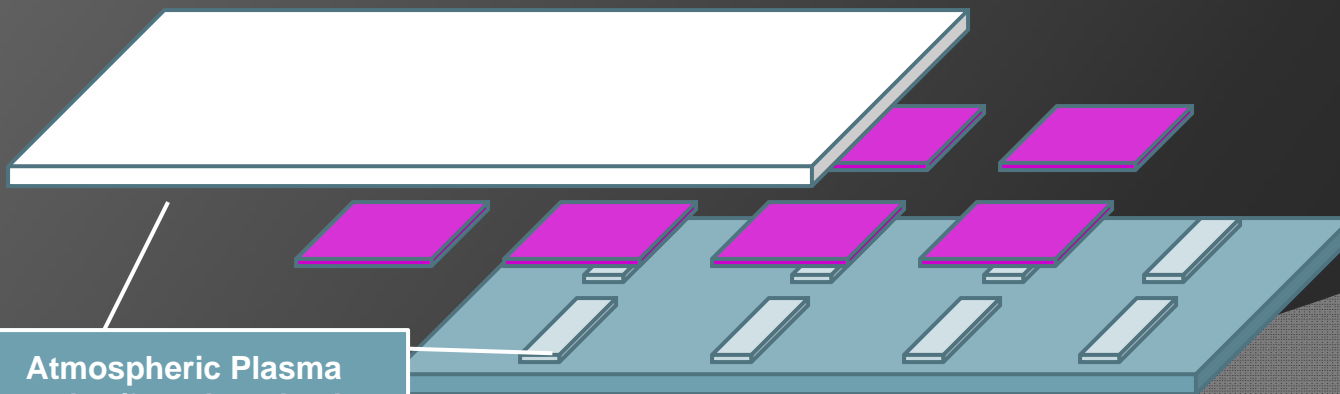
# Crystalline-Silicon (cSi) PV Module



- Anti-reflective layer
- SiO<sub>2</sub> layer
- Screen-printed Ag grid
- Pd layer
- Ti layer
- n-type silicon layer
- p-type silicon layer
- Metal/alloy back contact layer

Atmospheric Plasma cleaning/functionalization

# Monolithic PV Module



Glass / polymer encapsulation layer

PV cell layer

Roll-to-roll fabricated backsheet layer with patterned circuitry

Atmospheric Plasma cleaning/functionalization

# Triple Junction Roll-to-Roll Amorphous-Silicon (aSi) PV Module



- Screen-printed Ag grid layer
- Anti-reflective ITO layer
- p-type layer
- a-Si alloy layer
- n-type layer
- p-type layer
- a-SiGe alloy layer
- p-type layer
- a-SiGe alloy layer
- n-type silicon layer
- Silver & ZnO layer
- Metal/alloy back contact layer

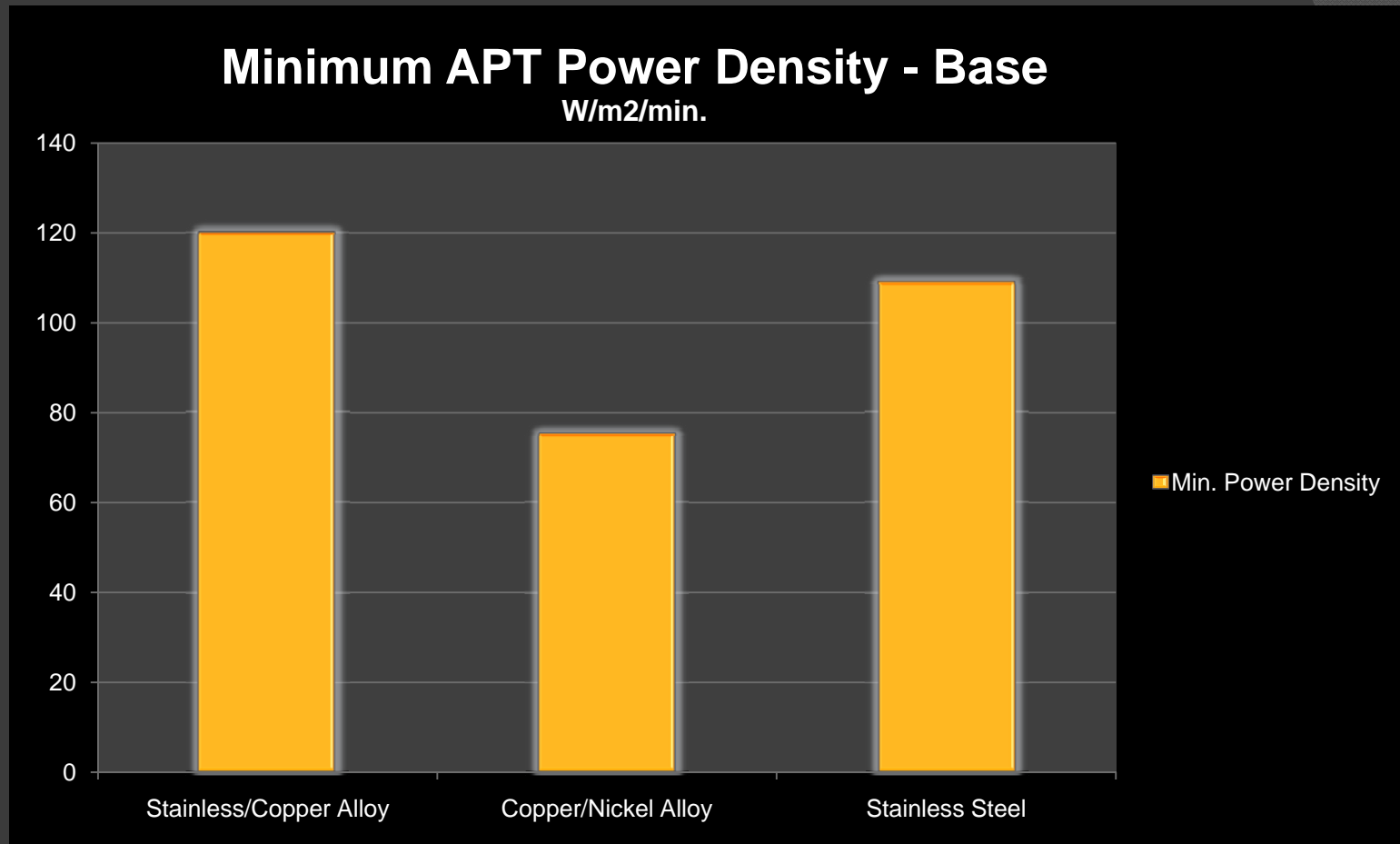
Atmospheric Plasma  
cleaning/functionalization

# Roll-to-Roll Organic PV Module



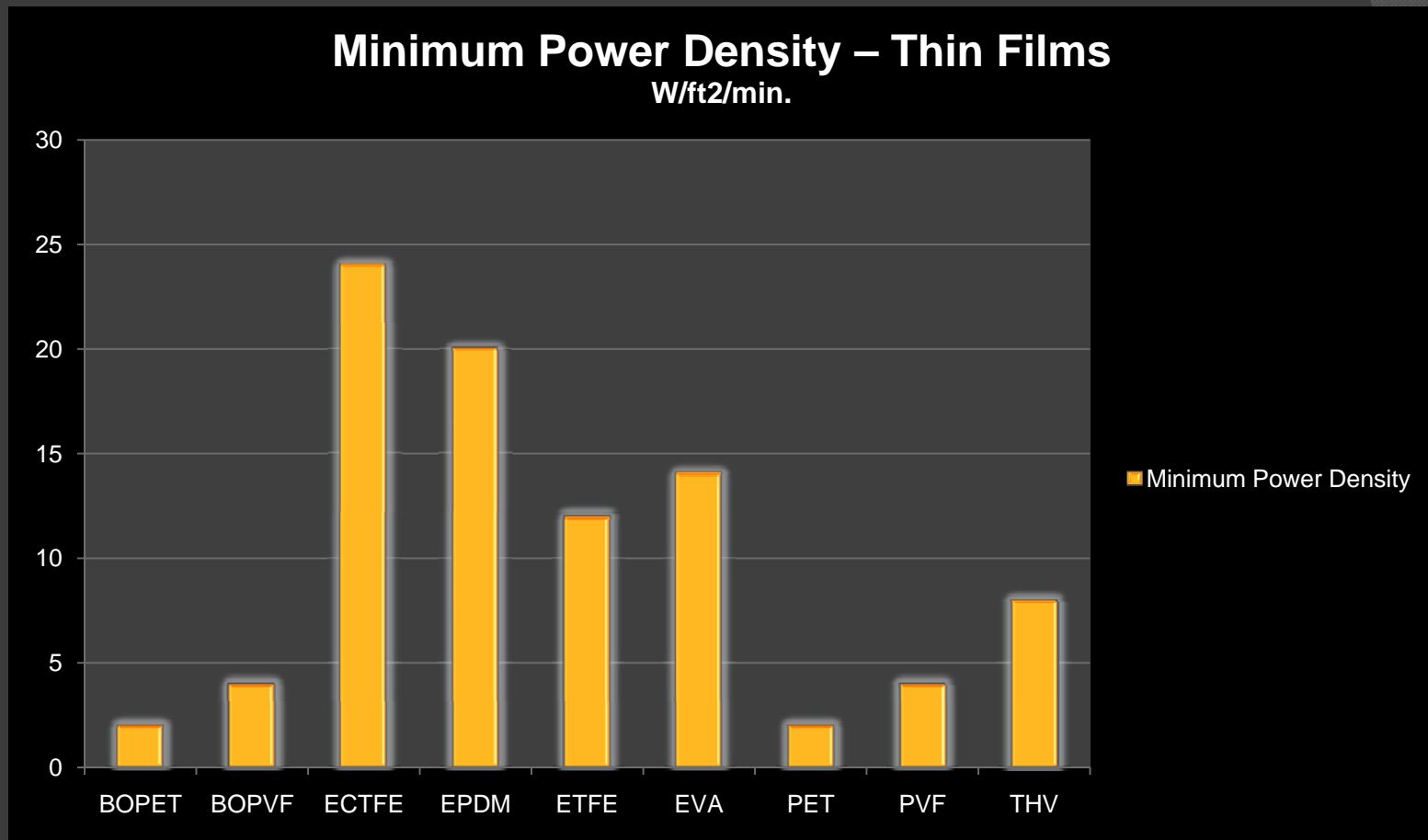
- Transparent top package / coating
- Transparent electrode
- Printed active material
- Primary electrode
- Metallized Polymer Film

# APT Prescriptions for Flexible PV - Base



**Note: Inert/Reactive gas proportions influence minimum power densities.**

# APT Prescriptions for Flexible PV – Thin Films

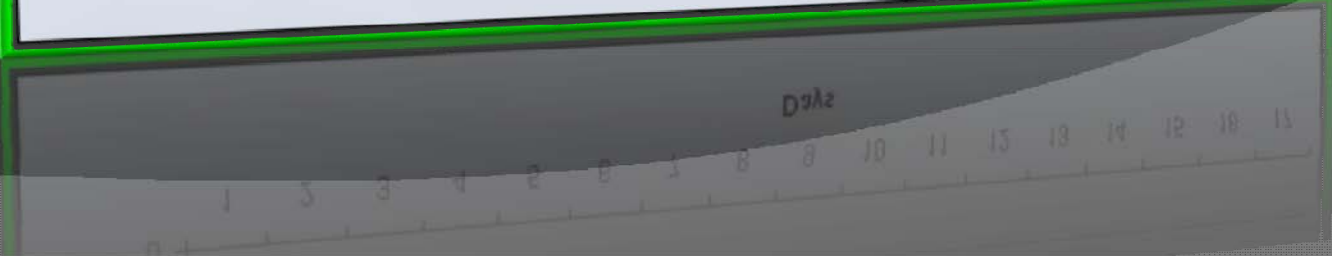
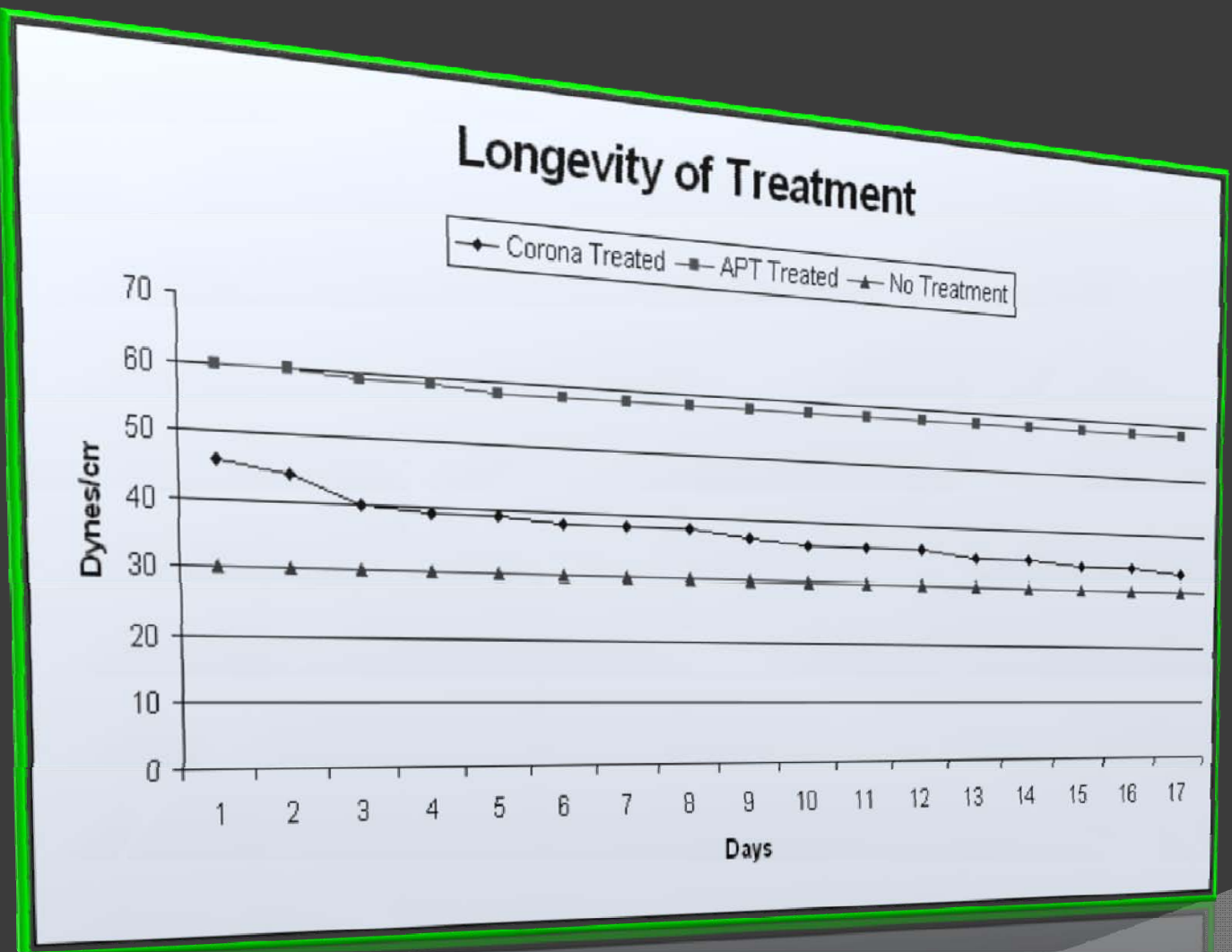


**Note: Inert/Reactive gas proportions influence minimum power densities.**

# APT Prescriptions for Flexible PV – Thin Films

<b>Substrate</b>	<b>Corona Watt Density (W/ft<sup>2</sup>/min.)</b>	<b>Corona Surface Tension (Dynes/cm)</b>	<b>Plasma Watt Density (W/ft<sup>2</sup>/min.)</b>	<b>Plasma Surface Tension (Dynes/cm)</b>
Polyimide	16.6	60	5.3 6.0	60 72
PLA	2.0	46	1.0 3.0	46 50
Tyvek®	2.0	54	1.0 2.0	46 60

# APT Prescriptions for Flexible PV – Thin Films



# APT Prescriptions for Flexible PV – Corona Issues

2x2 micron images of PET film

A. No Treatment



B. WD = 1.16W/ft<sup>2</sup>/min (12.5W/m<sup>2</sup>/min)



C. WD = 1.93W/ft<sup>2</sup>/min (20.8W/m<sup>2</sup>/min)

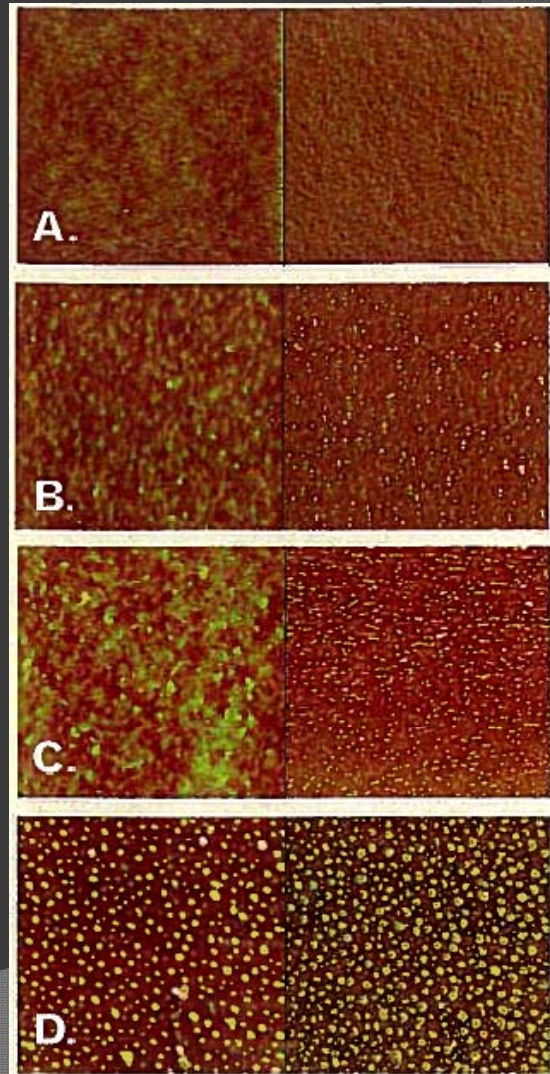


D. WD = 2.71W/ft<sup>2</sup>/min (29.2W/m<sup>2</sup>/min)



Topographical Image  
(Height – 10nm)

Phase Image  
(Range – 60°)



# APT Prescriptions for Flexible PV – Emissions

## Wet Vs. Dry Metal/Metal Alloy Cleaning

Metal Cleaning Process	➤ Chemical Wet Cleaning	➤ Atmospheric Plasma Dry Cleaning
Active Cleaning Agent(s)	<ul style="list-style-type: none"> <li>➤ Water-base Sulphuric Acid</li> <li>➤ Alkaline Solutions</li> <li>➤ Alcohol Solutions</li> <li>➤ Detergent Solutions</li> </ul>	<ul style="list-style-type: none"> <li>➤ Ion/Electron/Photon Bombardment</li> <li>➤ Inert + Oxygen Gas</li> </ul>
Dissolved within Chemical Agent(s)	<ul style="list-style-type: none"> <li>➤ Rolling Oils</li> <li>➤ Metal Oxides</li> <li>➤ Water-Soluble Metal Derivatives</li> </ul>	➤ n/a
Entrained in Process Exhaust	➤ n/a	<ul style="list-style-type: none"> <li>➤ Volatilized hydrocarbon particles</li> <li>➤ Aluminum oxide particles</li> <li>➤ Water-Soluble Aluminum Derivatives</li> </ul>
Emissions	➤ Water Laden w/ Chemical Wastes	<ul style="list-style-type: none"> <li>➤ 15 ppm Ozone</li> <li>➤ 2,336 ppm Inert gas (98%)</li> <li>➤ 185 ppm Reactive O<sub>2</sub> (70%)</li> <li>➤ &lt;10 ppm CO<sub>2</sub></li> <li>➤ &lt;10 ppm Water Vapor</li> <li>➤ Volatilized surface particulates</li> </ul>
Recurring Process Costs	<ul style="list-style-type: none"> <li>➤ Fresh Water, Additional Chemicals</li> <li>➤ Handling, Disposal Costs</li> </ul>	➤ Process Gases

# Conclusions

- **Vacuum Plasma Surface Modification**
  - **Anti-reflection**
  - **Surface passivation**
  - **Surface etching**
  - **Layer deposition**
- **Process Evolutions**
  - **Increasing chemical waste disposal issues**
  - **Module per unit process cost reductions**
- **Thin Film PV Cell Fabrication CAGR expected to be 74.8% to 2015.**

# Conclusions

- **Atmospheric (Dry) Plasma surface modification parameters (power density, gas chemistry) established for all flexible module components.**
- **Suitable for rigid module component surface preparation, such as frame and junction box sealing.**
- **In-line, continuous process**
- **No surface morphology effects**
- **Green technology, with no hazardous byproducts**

Thank you for attending...

Reducing Solar Module  
Cost with Atmospheric  
Plasma Surface  
Modification

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