Outline

- Megatrends & applications in packaging
  - Key markets & current drivers for transparent vacuum barrier films

- Key vacuum R2R processing technologies for the transparent barrier sector
  - Standard reactive evaporation of $\text{AlO}_x$
  - Plasma assisted reactive evaporation of $\text{AlO}_x$

- Clear barrier performance
  - Impact of plasma assistance
  - Tensile testing & impact on downstream processability

- Summary
Megatrends

- Changing brand awareness & customer perception
  - Cultural westernization driving single household, small volume packages
  - Emergence of “green” ecologically friendly brands & products with reduced CO₂ footprint
    - Sustainable & recyclable packaging

- Brands leveraging value chain to reduce cost
  - Definition of harmonized packaging formats
  - Material specification standardization

- Accelerated evolution in market driven requirements
  - Increased shelf life
  - Replacement of expensive, non-recyclable high CO₂ footprint Aluminum foil from laminates
  - Visibility of package content for the consumer
  - Change in form factor with migration from rigid packaging to flexible packaging
  - Down-gauging materials to provide the correct balance between package appearance, cost & mechanical rigidity
Motivation for Transparent “Ceramic” Barrier Adoption in Packaging

- Metallized polymer film sphere of application limited
  - No visibility of packaged product
  - Cannot be X-ray screened
  - Cannot be microwaved

- Enhanced performance when compared with traditional clear barriers
  - Low cost
  - Improved recyclability
  - Barrier layer thickness in nm range as opposed to µm range for wet processed PVdC & EVOH
  - Minimized barrier loss at high humidity levels

- Typical applications for ceramic barriers in packaging
  - Pouches for liquids, dry foods, sauce etc.
  - Sachets
  - Lidding materials for pasta, meats etc.
  - Medical, pharmaceutical & healthcare packaging
Global Market Volume Within Transparent Packaging

- Transparent ceramic oxide barrier market currently niche but growth outstripping traditional alternatives
  - EVOH market share ~ 52.5%
  - PVdC coated material market share ~ 43% with CAGR (2015) ~ -0.3%
  - Vacuum deposited transparent oxide market share ~ 4.4% with CAGR (2015) ~ 7.7%
    - 70% AlOx
    - 30% SiOx

Current Metal Oxide Vacuum Coating Market Size ~ 80,000-100,000 t/a

Source: Applied Materials Internal Estimate
Key R2R Processing Technology for the Clear Barrier Sector
**Transparent Aluminum Oxide Deposition Paths**

- **Standard AlO\textsubscript{x} evaporation**
  - Addition of oxygen gas to evaporated Al plume
  - Molecular oxygen weakly dissociated & incorporated at growth surface to result in growth of AlO\textsubscript{x} layer
  - Little control on AlO\textsubscript{x} layer density & morphology during growth & small process window for required stoichiometry

- **Plasma assisted AlO\textsubscript{x} evaporation**
  - High density oxygen plasma expands into evaporated Al plume
  - Molecular oxygen strongly dissociated & incorporated at growth surface
  - High degree of control of energetic particle flux to growth surface significantly expanding process window

![Diagrams of deposition paths](image)
Mechanism Behind Layer Morphology Improvement

- Plasma assisted deposition results in improved adsorbate mobility at the growth surface
  - Energetic particle flux substantially increased permitting “high surface temperature chemistry” at low substrate temperatures
    - Particle energy ~ 0.16 eV in traditional reactive AlO\textsubscript{x} deposition
    - Particle energy > 10 eV in plasma assisted AlO\textsubscript{x} deposition
  - Improved nucleation performance eliminating coating voids & reducing the thickness required for a continuous layer
Clear Barrier Performance
Impact of Plasma Assistance on Layer Morphology

- Clear migration from columnar growth structure to amorphous, grain free microstructure with high plasma density oxygen plasma within the deposition plume at high deposition rates (~100 nm/s)

**Standard**
Reactive AlO$_x$
Hardness ~ 3.2 GPA

**Medium Energy**
Plasma Assisted AlO$_x$
Hardness ~ 5.0 GPA

**High Energy**
Plasma Assisted AlO$_x$
Hardness ~ 6.0 GPA
Impact of Plasma Assistance on Layer Density

- Layer density increases considerably with increasing energetic particle flux
  - Measured using X-Ray reflectivity
  - Density increases by ~ 20% under high plasma density/current deposition conditions
  - Layer densities for high energetic fluxes approach sputtered stoichiometric Al₂O₃ values
    - Significant improvement observed when compared with conventional thermally evaporated AlOₓ layers
Void Defect Reduction Through Use of Plasma Assistance

- SEM analysis of AlO$_x$ layers prepared without and with plasma assistance show clear differences in void density
  - Standard AlO$_x$ layer shows higher void density during layer incubation phase close to the PET substrate interface
  - Plasma assisted AlO$_x$ void density significantly lower & more evenly distributed throughout layer

AlO$_x$ layer, deposited without plasma
Average void size ~ 13.6 nm
Average void density ~ 12 x higher than with plasma

AlO$_x$ layer, deposited with plasma
Average void size ~ 15 nm
Impact of Defects on Barrier Performance

- Defects in AlOₓ layer impact permeation
  - Permeation rate increases with square of the defect radius
  - Crank diffusion calculations based on measured void size & density used to predict difference in standard & plasma assisted AlOₓ water vapor diffusivity
    - Defect size & spacing result in ~ 2.5 x lower permeation rates for plasma assisted AlOₓ compared with standard evaporation!
    - Correlates well with experimental data (see following slides)

\[
D_{\text{Eff (AlO}_x\text{)}} = D_{\text{Substrate Void}} + D_{\text{AlO}_x f_{\text{Bulk}}}
\]

Defect Area = \( \pi r^2 \)
Impact of Plasma Source Drive Current on Performance

- Hollow cathode source drive current strongly impacts barrier performance on a broad range of substrates
  - WVTR decreases with increased current irrespective of substrate material used
  - Increasing energetic particle flux incident at substrate surface substantially impacts both nucleation & growth process
  - Substrate surface energies no longer plays significant role on defining AlO$_x$ thickness required for dense, void free layer deposition
Impact of Layer Thickness for AlOx on PET

- Barrier performance initially improves with increased layer thickness prior to saturation
  - Dependent primarily on AlO$_x$ surface coverage
  - Typical food packaging barrier layers ~ 10-15 nm in thickness dependent on application
  - AlO$_x$ barrier layers ~ 10 nm thick preferred for mechanical crack resistance during handling & downstream processing
Factors Impacting Tensile Failure

- Defect size, \((2l)\), impacts stress required to induce brittle fracture in \(\text{AlO}_x\) layer
  - Critical stress similar for both standard & plasma assisted \(\text{AlO}_x\) layer but lower for standard AlOx due to reduced hardness/elastic modulus

- Reduced void density eliminates mechanically weak stress concentration zones within coating thickness
  - Weibull modulus increases with reduction in void density
    - Plasma assisted \(\text{AlO}_x\) = high Weibull modulus
    - Standard \(\text{AlO}_x\) = low Weibull modulus
  - Significant impact on tensile strength & resultant improved tensile reliability for plasma assisted \(\text{AlO}_x\)

\[
\sigma_{\text{Critical}} = \left(\frac{2E\gamma_{\text{AlO}_x}}{\pi l}\right)^{1/2}
\]

\[
F = 1 - \exp\left(-\left(\frac{\sigma_{\text{bend}}}{\sigma_{\text{critical}}^m}\right)^n\right)
\]

- \(F\): Failure probability
- \(\sigma_{\text{bend}}\): Bend stress
- \(\sigma_{\text{critical}}\): Critical stress
- \(n\): Number of flaws
- \(d_{\text{film}}\): Film thickness
Impact of Plasma Assistance on Mechanical Durability

- **Plasma assisted AlO$_x$ deposition on PET show ~ 60% improvement** in mechanical durability/critical strain & barrier performance compared with reactive AlO$_x$
  - Critical strain inherent to quality of AlO$_x$ layer itself rather than substrate (critical strain on PET $\approx$ critical strain on BOPP)
  - Initial slow degradation in barrier performance = crack generation in direction orthogonal to applied stress
  - Rapid barrier performance degradation = unstable crack generation & propagation in direction of applied stress (catastrophic failure)
  - Standard AlO$_x$ layer barrier $\sim$ 50% higher than for plasma assisted AlO$_x$
Critical Radius of Curvature vs Critical Strain

- Consider simple bi-layer system
  - $\text{AlO}_x$ on BOPP with critical strain values measured
  - Critical radius to fracture strong function of thickness ratio & elastic modulus ratio

\[
R_{\text{critical}} = \left( \frac{h_{\text{AlO}_x} + h_{\text{BOPP}}}{2\varepsilon_{\text{critical}}} \right) \left( \frac{1 + 2\eta + \chi\eta^2}{(1 + \eta)(1 + \chi\eta)} \right) \approx \left( \frac{h_{\text{BOPP}}}{2\varepsilon_{\text{critical}}} \right)
\]

\[\eta = \frac{h_{\text{AlO}_x}}{h_{\text{BOPP}}} \quad \chi = \frac{E_{\text{AlO}_x}}{E_{\text{BOPP}}}\]

- For 10 nm $\text{AlO}_x$ layer on 12 µm thick BOPP substrate
  - Standard $\text{AlO}_x$ layer critical radius ~ 0.41 mm
  - Plasma assisted $\text{AlO}_x$ layer critical radius ~ 0.29 mm
  - Substrate stiffness controls ease of handling in tools (reduced wrinkling rather than crack generation)

- $\text{AlO}_x$ layer & substrate thickness to be minimized to improve crack resistance
- Plasma assisted $\text{AlO}_x$ layer more mechanically robust than standard evaporated $\text{AlO}_x$
Impact of AlO$_x$ Conversion on Performance

- 10 nm thick AlO$_x$ layers post-processed using gravure topcoat & lamination to determine suitability for use in pouch
  - Gravure topcoat provides mechanical protection of “ceramic” barrier layer
  - WVTR shows considerable improvement in laminated package form for plasma assisted AlO$_x$
  - Standard AlO$_x$ cracks during Gelbo flex test & water barrier performance is partially lost
  - Plasma assisted AlO$_x$ shows increased crack resistance & small deterioration in barrier performance level after Gelbo flex test

<table>
<thead>
<tr>
<th>Step</th>
<th>Normalized WVTR (Standard)</th>
<th>Normalized WVTR (Plasma)</th>
<th>Norm. OTR (Standard)</th>
<th>Norm. OTR (Plasma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Deposited</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>Topcoated</td>
<td>25%</td>
<td>18%</td>
<td>8%</td>
<td>6%</td>
</tr>
<tr>
<td>Laminated</td>
<td>25%</td>
<td>9%</td>
<td>8%</td>
<td>6%</td>
</tr>
<tr>
<td>Gelbo Test</td>
<td>65%</td>
<td>14%</td>
<td>Not Measured</td>
<td>Not Measured</td>
</tr>
</tbody>
</table>

Plasma assisted AlO$_x$ provides required stability for implementation in broad range of pouch designs
Summary
Summary

- Plasma assisted AlO_x deposition show clear performance advantages compared with standard, reactively evaporated AlO_x layers on PET & BOPP
  - Barrier performance levels improved by $\geq 50\%$
  - Void density in bulk plasma assisted AlO_x layer $\sim 90\%$ lower than for standard reactively evaporated layer
  - Critical radii before fracture $\sim 40\%$ lower = improved downstream processability & yield
  - Converted plasma assisted AlO_x layer shows significant retention of barrier performance following addition of topcoat & lamination
  - Mechanical performance of plasma assisted AlO_x layer well suited for high stress applications including pouches & sachets

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Uncoated WVTR</th>
<th>Standard AlO_x WVTR</th>
<th>Plasma Assisted AlO_x WVTR</th>
<th>Uncoated OTR</th>
<th>Standard AlO_x OTR</th>
<th>Plasma Assisted AlO_x OTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET (12 µm)</td>
<td>40-50</td>
<td>$\leq 0.7$</td>
<td>$\leq 0.35$</td>
<td>100-140</td>
<td>$\leq 1.6$</td>
<td>$\leq 0.8$</td>
</tr>
<tr>
<td>BOPP (20 µm)</td>
<td>4-9</td>
<td>$\leq 7$</td>
<td>$\leq 0.30$</td>
<td>2000-2500</td>
<td>$\leq 50$</td>
<td>$\leq 35$</td>
</tr>
</tbody>
</table>