Improving the Performance of Ceramic Barrier Layers used in Packaging Materials

Roland Trassl
Senior Manager Advanced Development
Applied Materials WEB Coating GmbH

AIMCAL Tampa, Florida, USA

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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 AlO_x
  - Plasma assisted reactive evaporation of AlO_x
- Clear barrier performance
  - Impact of plasma assistance
  - Tensile testing & impact on downstream processability
- Summary

Megatrends & Applications in Packaging

Megatrends

- Changing brand awareness & customer perception
  - Cultural westernization driving single household, small volume packages
  - Emergence of “green” ecologically friendly brands & products with reduced CO_2 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 CO_2 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

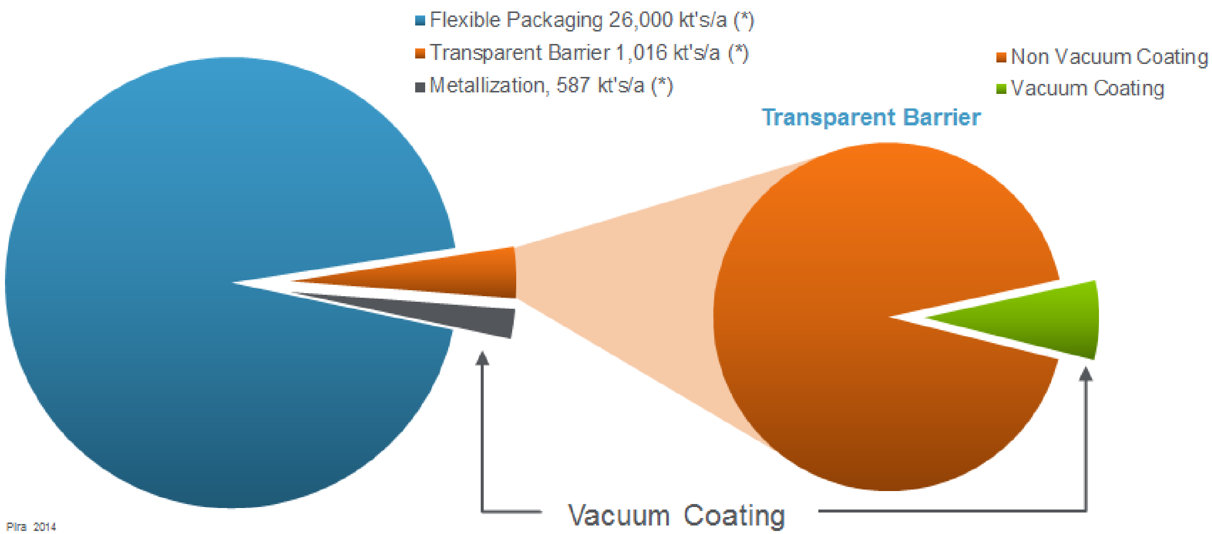
- Typical applications for ceramic barriers in packaging
  - Pouches for liquids, dry foods, sauce etc.
  - Sachets
  - Lidding materials for pasta, meats etc.
  - Medical, pharmaceutical & healthcare packaging

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 % AlO_x**
    - **30 % SiO_x**

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

Source: Applied Materials Internal Estimate



(*) Smithers Pira 2014

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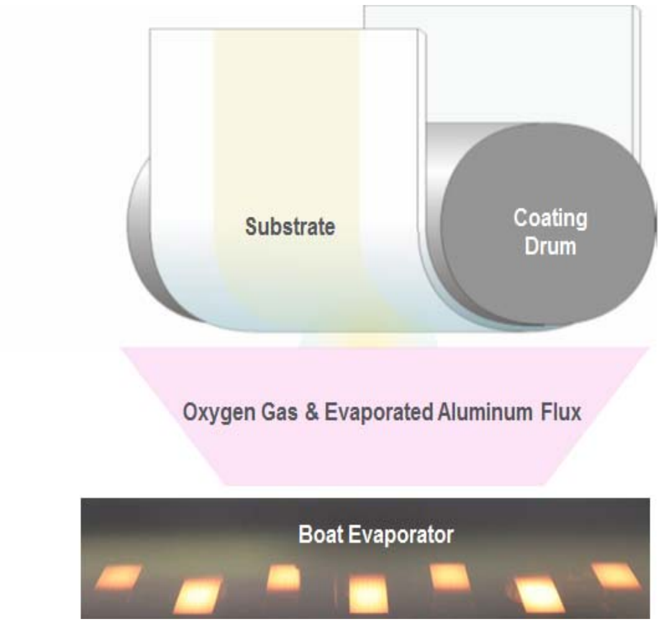
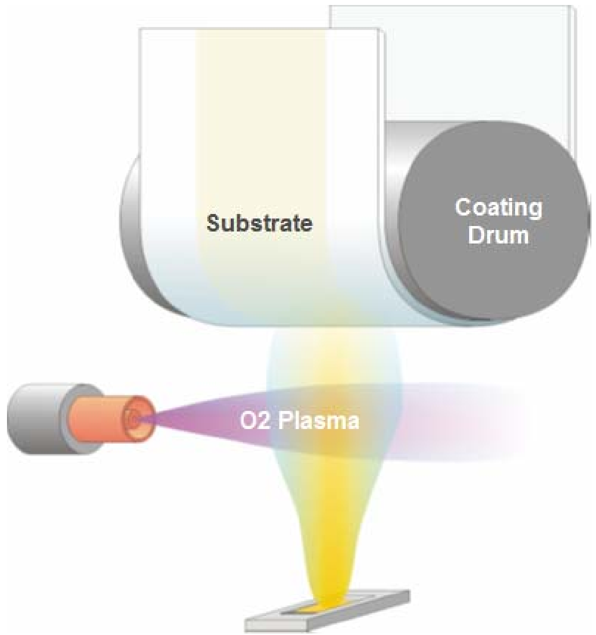
Key R2R Processing Technology for the Clear Barrier Sector

Transparent Aluminum Oxide Deposition Paths

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

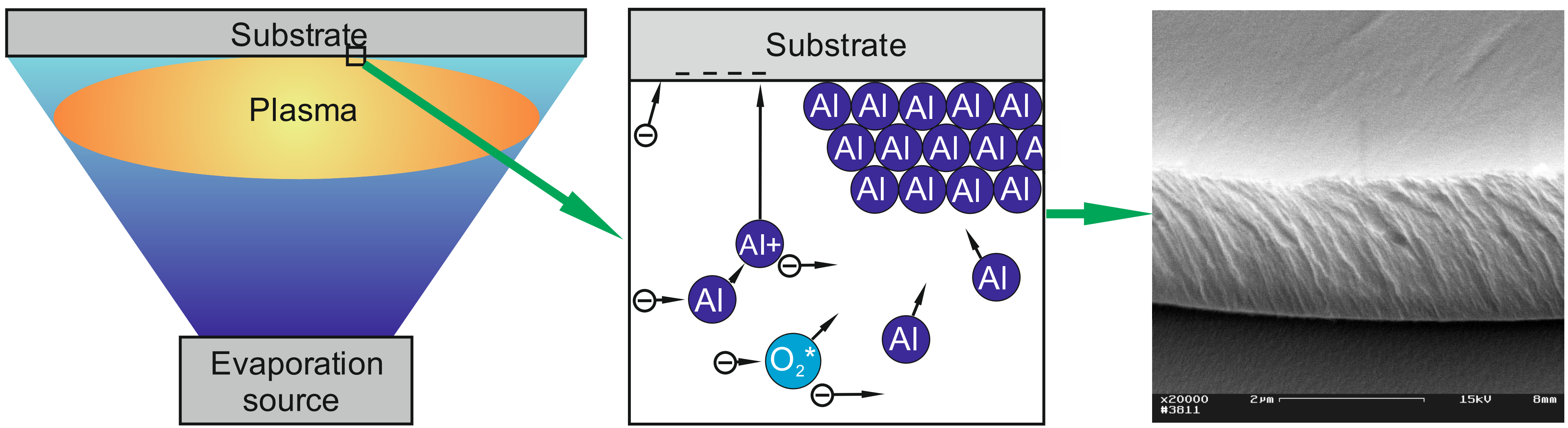


- Plasma assisted AlO_x evaporation
  - High density oxygen plasma expands into evaporated Al plume
  - Molecular oxygen strongly dissociated & incorporated at growth surface
  - High degree of control of **energetic** particle flux to growth surface significantly expanding process window



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_x deposition
    - Particle energy > 10 eV in plasma assisted AlO_x deposition
  - Improved nucleation performance eliminating coating voids & reducing the thickness required for a continuous layer



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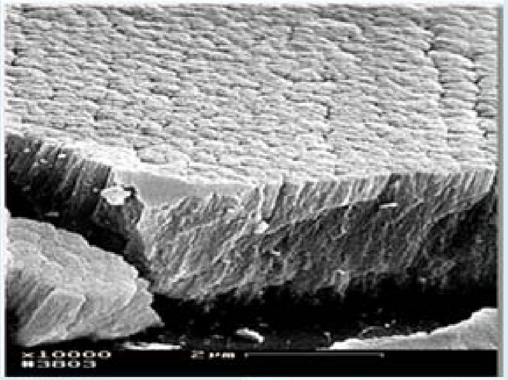
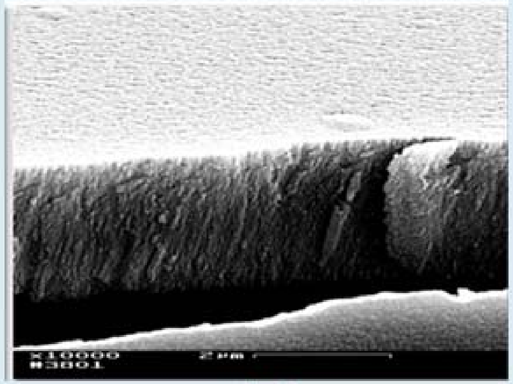
Clear Barrier Performance

Impact of Plasma Assistance on Layer Morphology

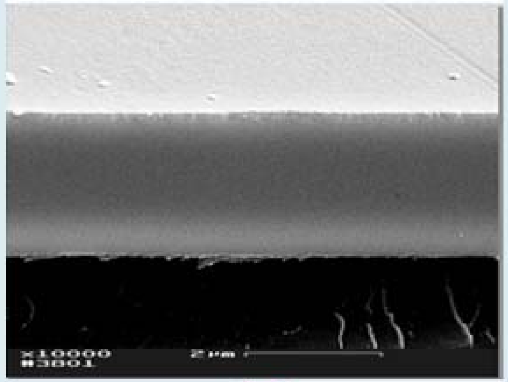
- Clear migration from columnar growth structure to amorphous, grain free microstructure with high plasma density oxygen plasma within the deposition plume at high deposition rates (~100 nm/s)



Standard
Reactive AlO_x
Hardness ~ 3.2 GPa



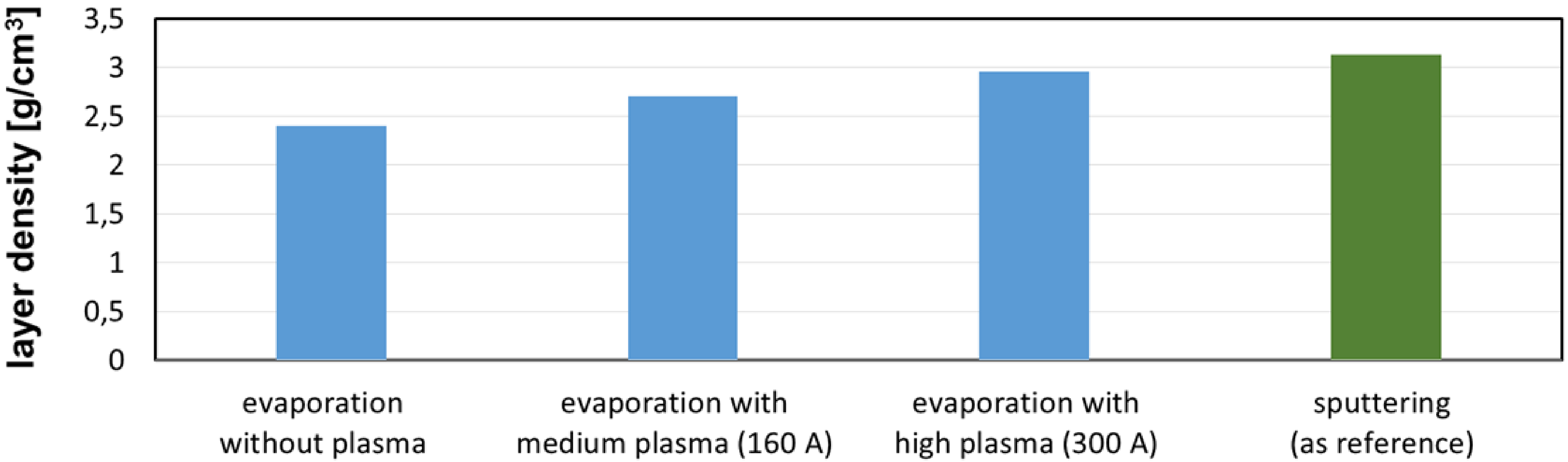
Medium Energy
Plasma Assisted AlO_x
Hardness ~ 5.0 GPa



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 Al_2O_3 values**
    - Significant improvement observed when compared with conventional thermally evaporated AlO_x layers



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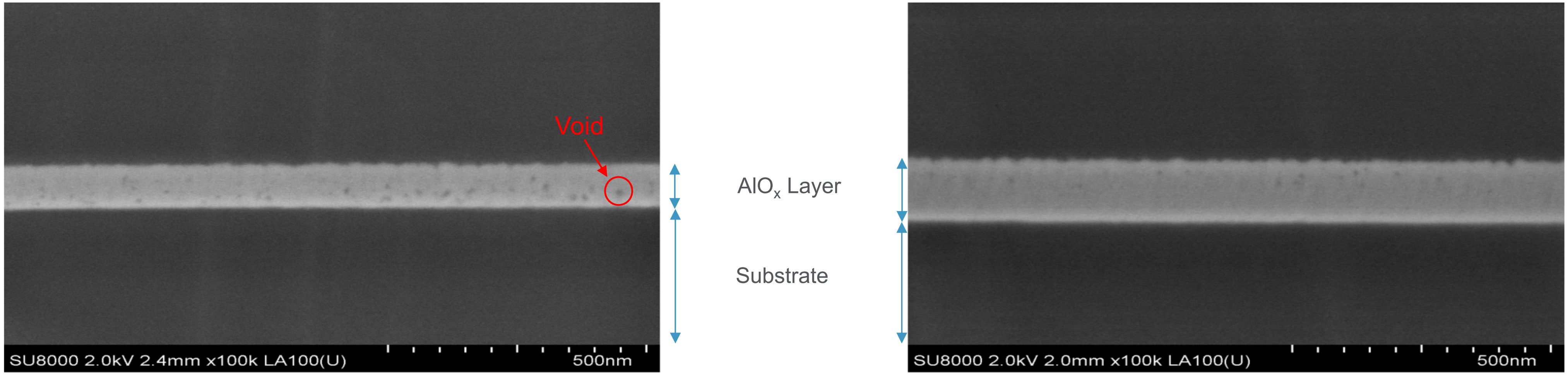
Void Defect Reduction Through Use of Plasma Assistance

- 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 thoughout 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

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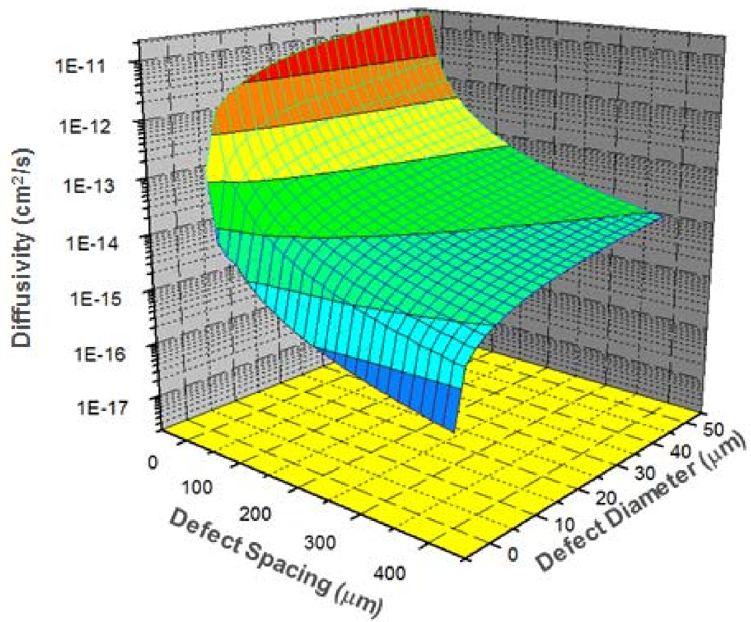
Impact of Defects on Barrier Performance

- Defects in AlO_x 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 AlO_x water vapor diffusivity
    - **Defect size & spacing result in ~ 2.5 x lower permeation rates for plasma assisted AlO_x compared with standard evaporation!**
    - Correlates well with experimental data (see following slides)



$$D_{Eff\,(AlO_x)} = D_{Substrate} f_{Void} + D_{AlO_x} f_{Bulk}$$

Defect Area = πr^2

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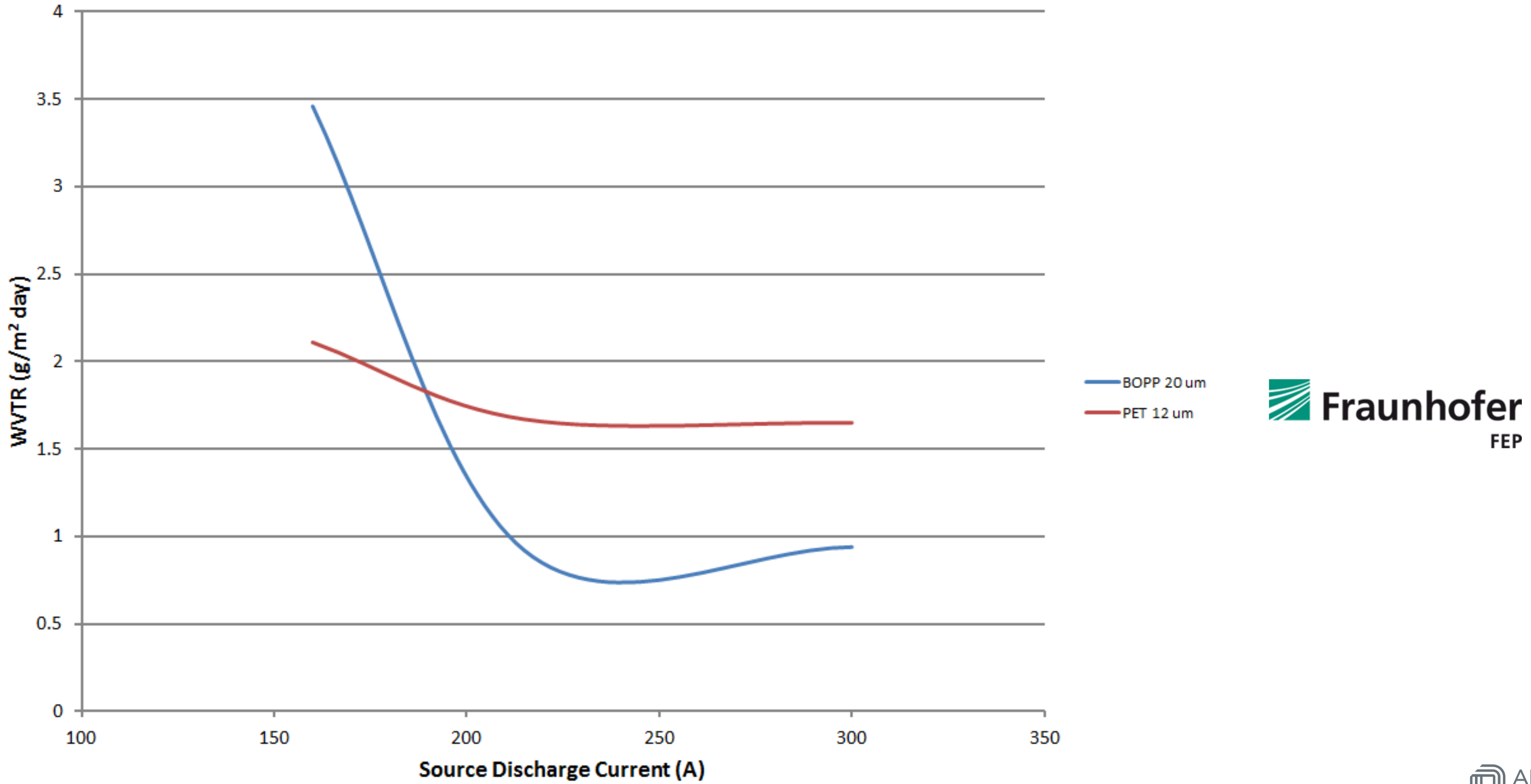
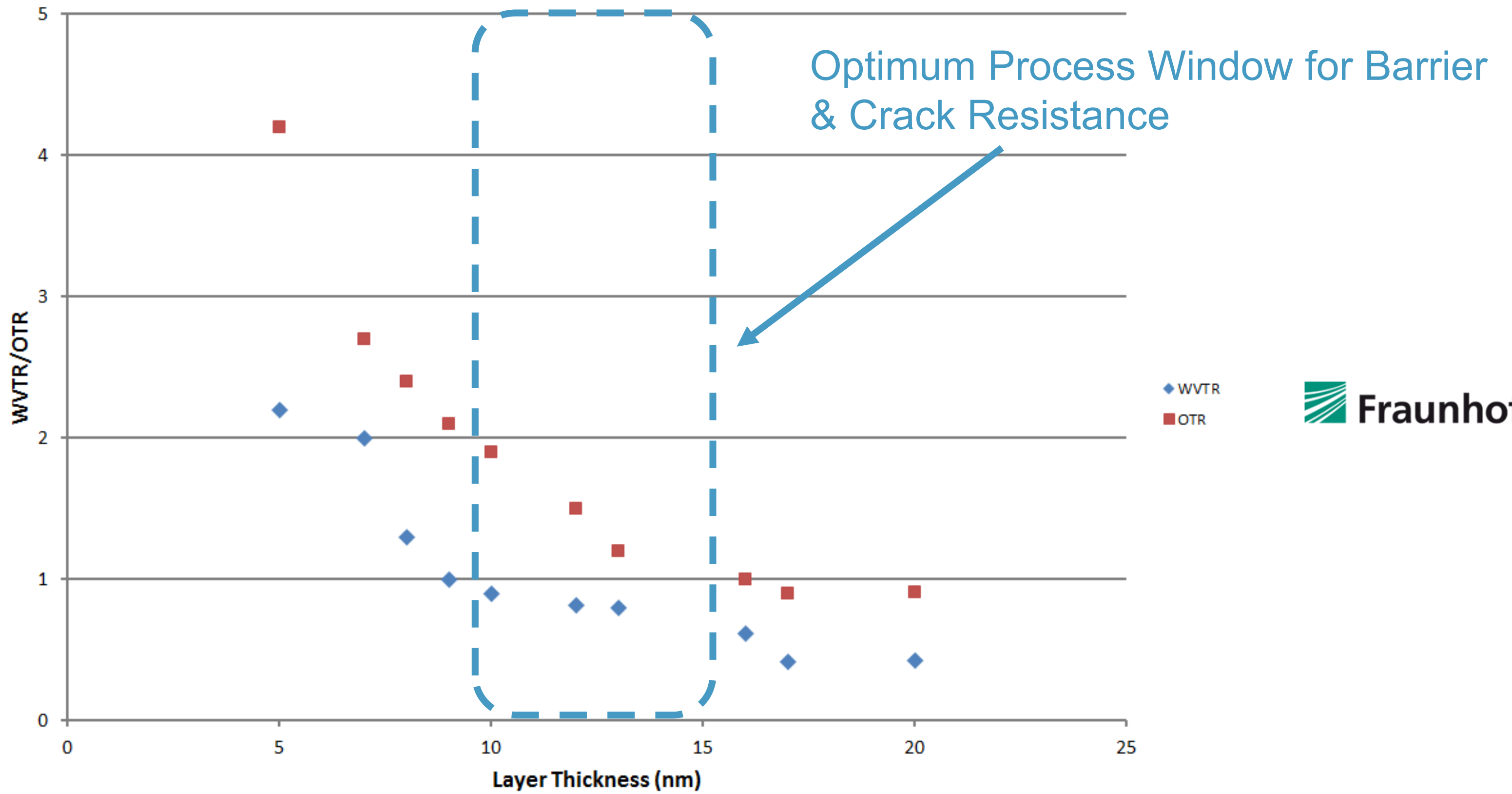
Impact of Plasma Source Drive Current on Performance

- 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



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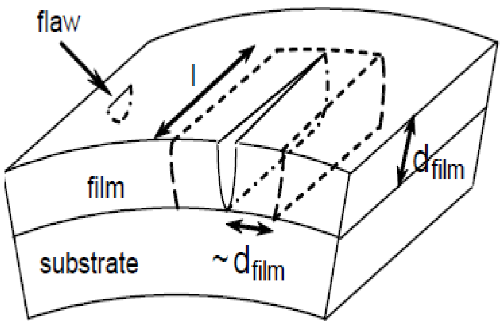
Factors Impacting Tensile Failure

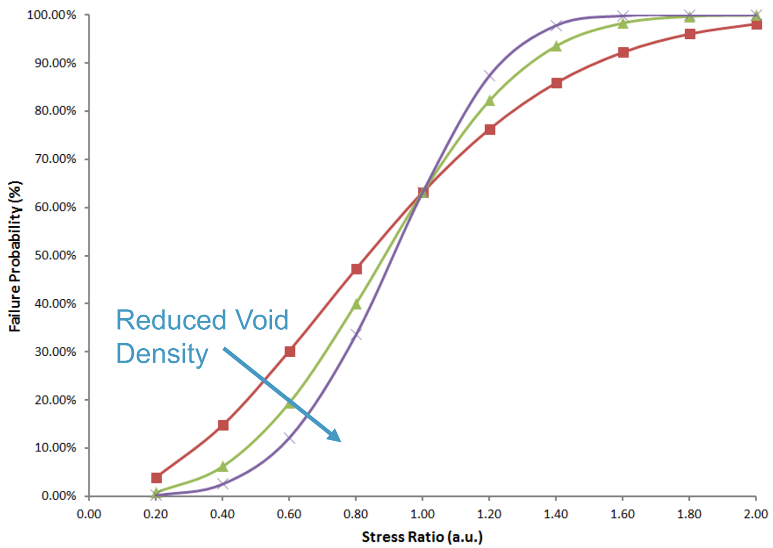
$$\sigma_{Critical} = \left(\frac{2E\gamma_{AlO_x}}{\pi l} \right)^{1/2}$$

- Defect size, (2*l*), impacts stress required to induce brittle fracture in AlO_x layer
  - Critical stress similar for both standard & plasma assisted 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 AlO_x = high Weibull modulus
    - Standard AlO_x = low Weibull modulus
  - Significant impact on tensile strength & resultant improved tensile reliability for plasma assisted AlO_x



$$F = 1 - \exp\left(- \left(\frac{\sigma_{bend}}{\sigma_{critical}} \right)^m \right)$$



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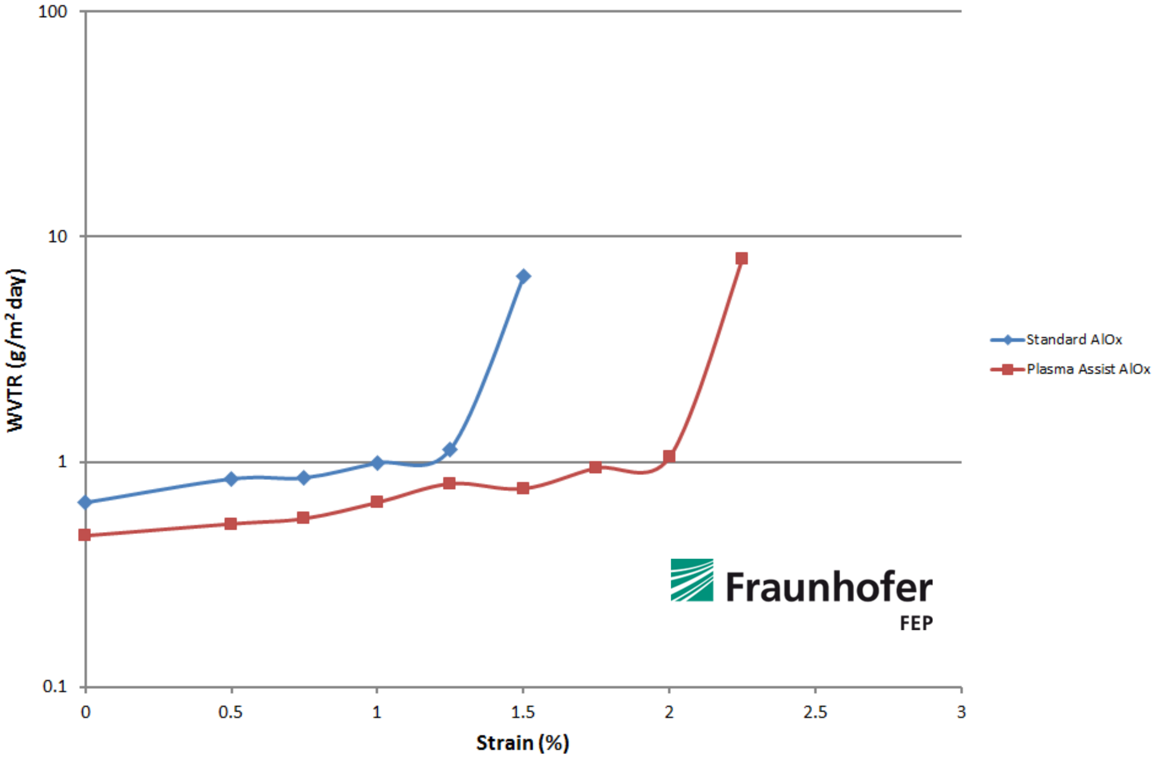
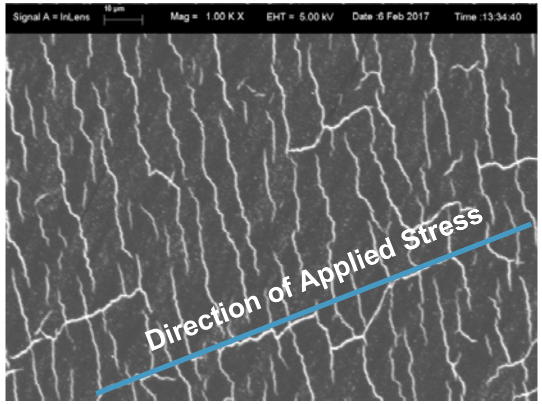
Impact of Plasma Assistance on Mechanical Durability

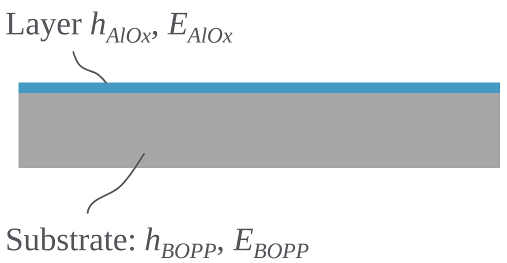
- **Plasma assisted AlO_x deposition on PET show ~ 60% improvement** in mechanical durability/critical strain & barrier performance compared with reactive AlO_x
  - Critical strain inherent to quality of AlO_x layer itself rather than substrate (critical strain on PET ≈ critical strain on BOPP)
  - Initial 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 ~ 50% higher than for plasma assisted AlO_x





Critical Radius of Curvature vs Critical Strain

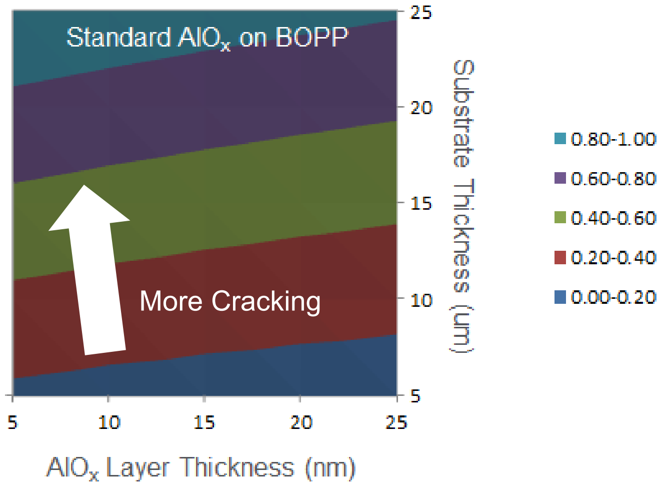
- Consider simple bi-layer system
  - AlO_x on BOPP with critical strain values measured
  - Critical radius to fracture strong function of thickness ratio & elastic modulus ratio

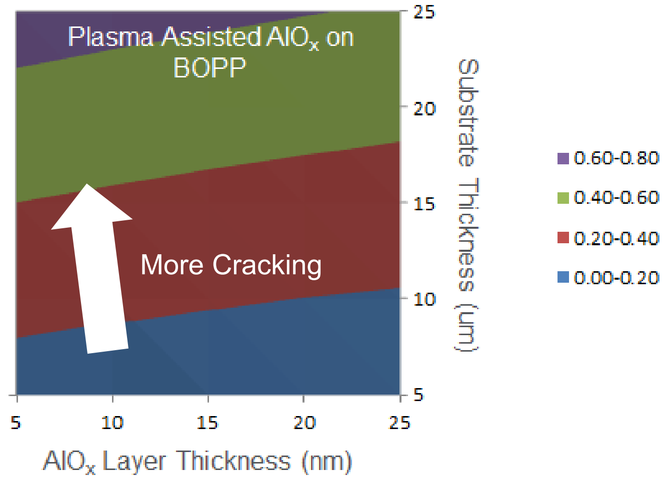


$$R_{critical} = \left(\frac{h_{AlO_x} + h_{BOPP}}{2\varepsilon_{critical}}\right)\left(\frac{1+2\eta+\chi\eta^2}{(1+\eta)(1+\chi\eta)}\right) \approx \left(\frac{h_{BOPP}}{2\varepsilon_{critical}}\right) \qquad \eta = \frac{h_{AlO_x}}{h_{BOPP}} \qquad \chi = \frac{E_{AlO_x}}{E_{BOPP}}$$

  - For 10 nm AlO_x layer on 12 µm thick BOPP substrate
    - Standard AlO_x layer critical radius ~ 0.41 mm
    - Plasma assisted AlO_x layer critical radius ~ 0.29 mm
    - Substrate stiffness controls ease of handling in tools (reduced wrinkling rather than crack generation
  - **AlO_x layer & substrate thickness to be minimized to improve crack resistance**
  - **Plasma assisted AlO_x layer more mechanically robust than standard evaporated AlO_x**

Critical Radius Contour Map in mm





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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

Step	Normalized WVTR (Standard)	Normalized WVTR (Plasma)	Norm. OTR (Standard)	Norm. OTR (Plasma)
As Deposited	100%	100%	100%	100%
Topcoated	25%	18%	8%	6%
Laminated	25%	9%	8%	6%
Gelbo Test	65%	14%	Not Measured	Not Measured

Plasma assisted AlO_x provides required stability for implementation in broad range of pouch designs

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Summary

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- **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 ≥ 50%
  - Void density in bulk plasma assisted AlO_x layer ~ 90% lower than for standard reactively evaporated layer
  - Critical radii before fracture ~ 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

Substrate	Uncoated WVTR	Standard AlO_x WVTR	Plasma Assisted AlO_x WVTR	Uncoated OTR	Standard AlO_x OTR	Plasma Assisted AlO_x OTR
PET (12 µm)	40-50	≤ 0.7	≤ 0.35	100-140	≤ 1.6	≤ 0.8
BOPP (20 µm)	4-9	≤ 7	≤ 0.30	2000-2500	≤ 50	≤ 35

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