Progress in Roll-to-Roll Atomic Layer Deposition

Council for Chemical Research
Barrier Workshop
Arlington, Virginia
September 20, 2012

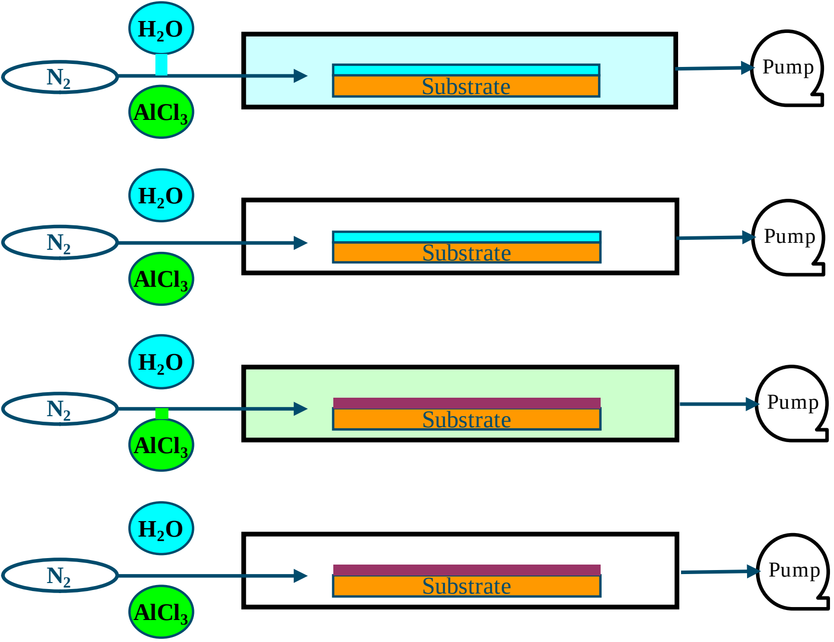
E. Dickey
Lotus Applied Technology

Outline

- ALD for barrier films
- ALD based on substrate translation – cost reduction and compatibility with R2R processing
- Approaches based on substrate translation
- Challenges for scaling (and possible solutions)
- Status of commercialization and outlook

Conventional Pulse-Based ALD

- Defined by sequential half-reactions at surface
  - Saturation characteristics key to ALD's unique attributes
- Most ALD reactions defined by 4 steps in a cycle



Mono-Molecular Layer of water is adsorbed

Water vapor is purged from reaction chamber

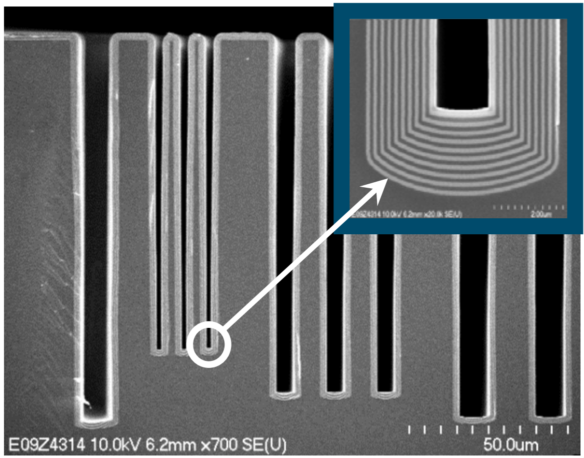
$AlCl_3$ reacts with water to form Al_2O_3, with HCl as vapor by-product

$AlCl_3$ and HCl vapors purged, leaving < 1 monomolecular layer of Al_2O_3

This cycle is repeated until desired thickness is reached

ALD’s Unique Advantages for Barriers

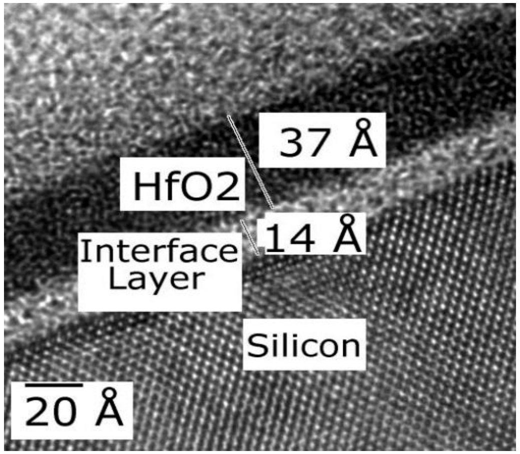
Extreme Conformality



Alternating Al2O2/Ta2O5 in deep Si trench

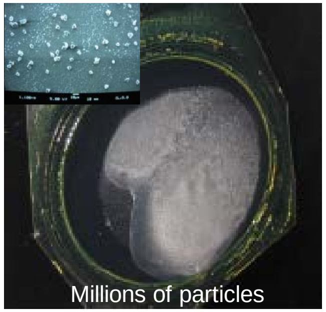
- ALD can coat into and around substrate defects
- Surface-limited growth leads to continuous films at very low thickness
- High film density achieved with very low stress

Continuous pinhole-free very thin films



Continuous “Hi-k” dielectric

Massive Scratching



Millions of particles

WVTR in10^{-3} range for both of these samples!

Pulse-Based ALD Limitations

- Pulse-based ALD is very slow
  - Completion of full 4-step cycle generates only ~ 1Å thickness
- Historically, ALD commercial applications limited to products that demand extreme performance and command high prices
  - TFEL displays (niche market)
    - $15,000 per square meter
  - Leading edge IC’s
    - Up to $1,000,000 per square meter

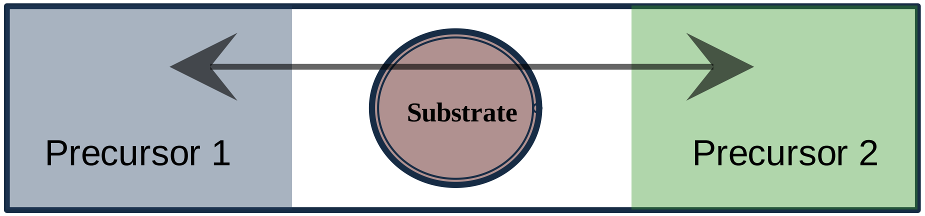
- ***R2R processing with pulse-based ALD not really practical***

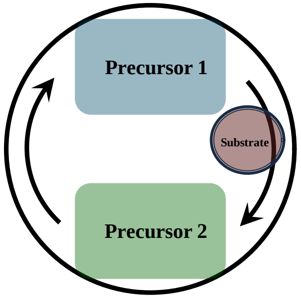
ALD by Substrate Translation

AKA “Spatial” ALD, “Continuous” ALD

Instead of pulsing the precursors onto the substrate,
move the substrate to the precursors

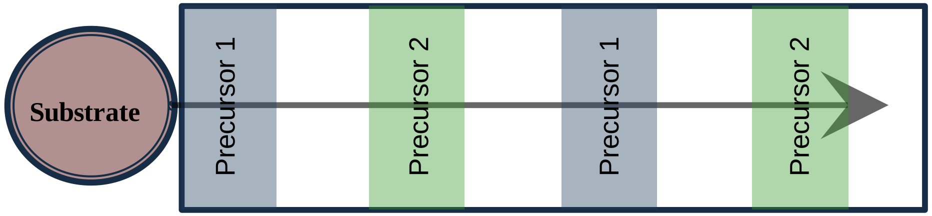
Move back and forth between two precursor zones





OR

Pass through individual cycle elements in sequence



Potential Advantages

- Relies on substrate motion - Directly compatible with R2R processing
- High coating rates – lower cost
  - Time required for precursor introduction, saturation, and purge are eliminated from the ALD cycle
- ***Coating only occurs on the substrate (and carrier, if used)***
- High precursor utilization
  - Precursors may be trapped and recycled prior to combining in pumping line
- Process control greatly simplified compared to other R2R deposition techniques
  - Wide tolerance to variation in precursor flux, web speed, etc.

ALD By Substrate Translation

A brief history

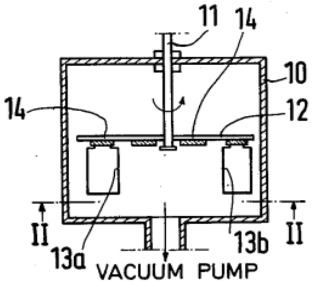


FIG. 1

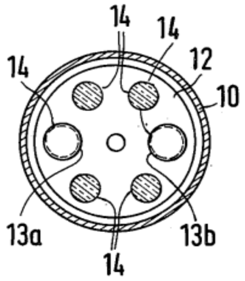


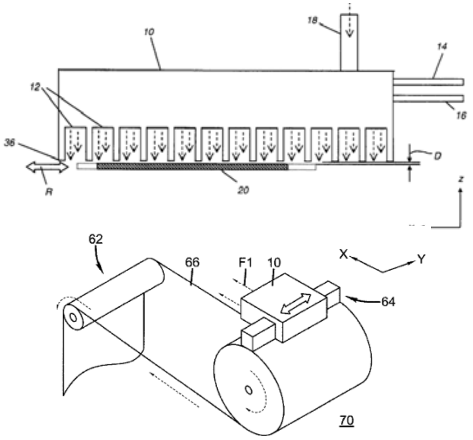
FIG. 2

- *Not new* - Substrate translation illustrated in original ALD patent (1977)

- Briefly explored as method for producing thin film EL phosphor
  - Evaporation of elemental zinc and sulfur
- Mostly dormant concept since invention
- Resurgent interest beginning in just the last few years
  - More than a half dozen groups with substantial programs underway

Precursor Separation Methods

- Atmospheric pressure processes
  - High pressure and precision small gaps used to prevent precursor interaction
    - Pioneered by Kodak
    - Several other organizations now also innovating on this concept



Images from Levy patent (Kodak)

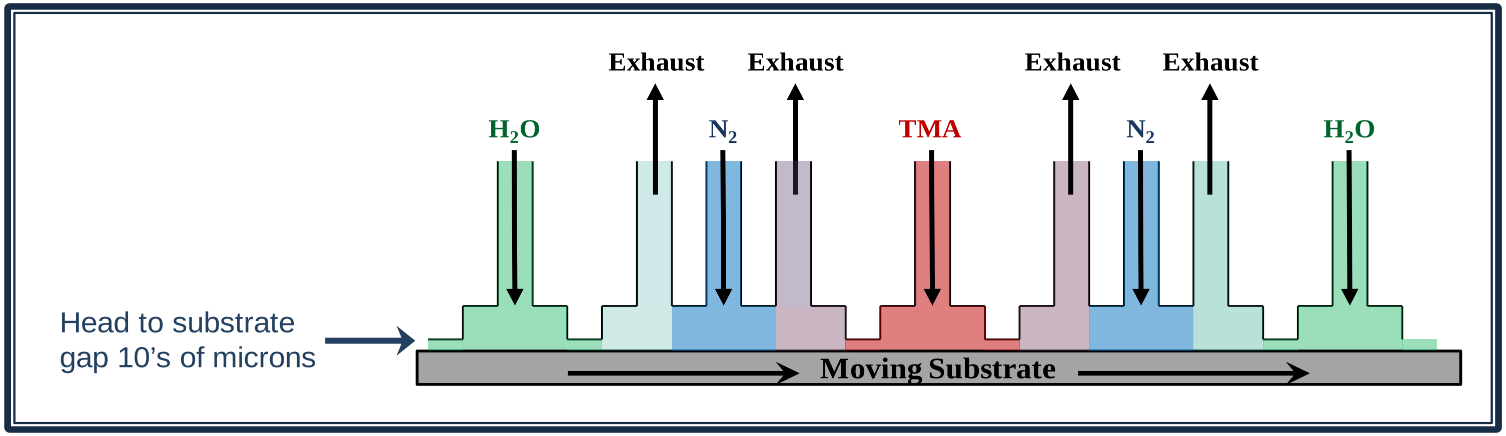
- Vacuum based processes
  - Process pressure similar to that used for conventional pulse-based ALD
  - Precursors separated using differential pressure, pumping

Thin Film System TFS 200R for continuous mode ALD research

“Roll to Roll Research” reactor from Beneq, Oy

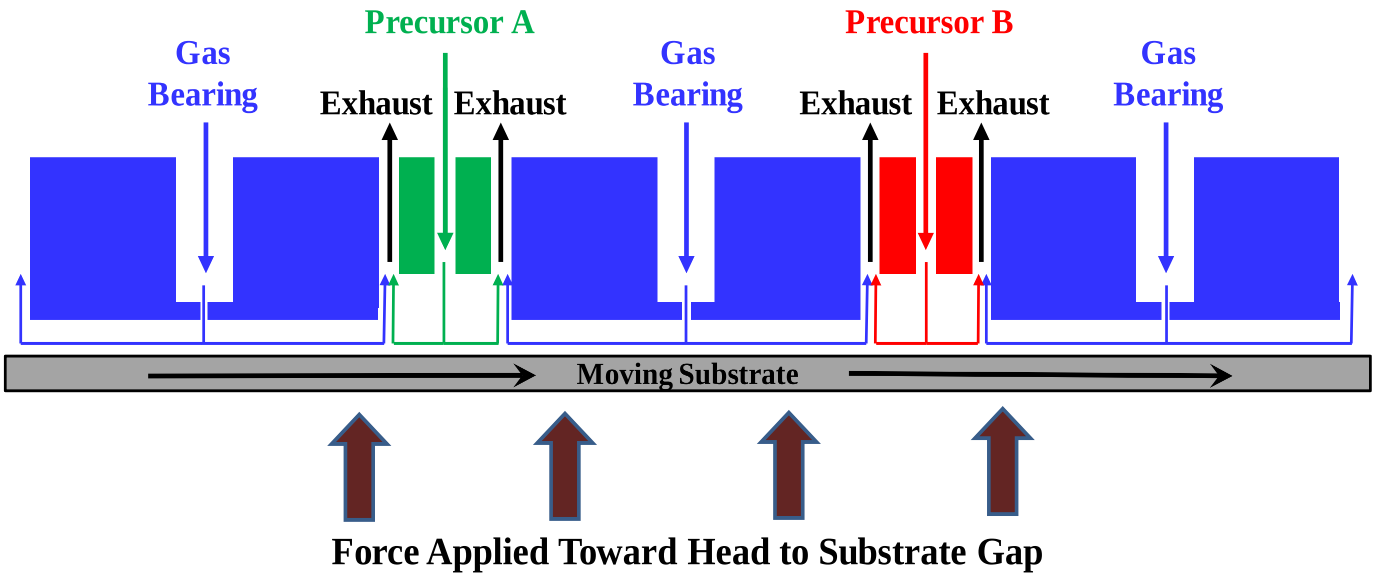
Atmospheric Pressure

Mechanical Head Spacing



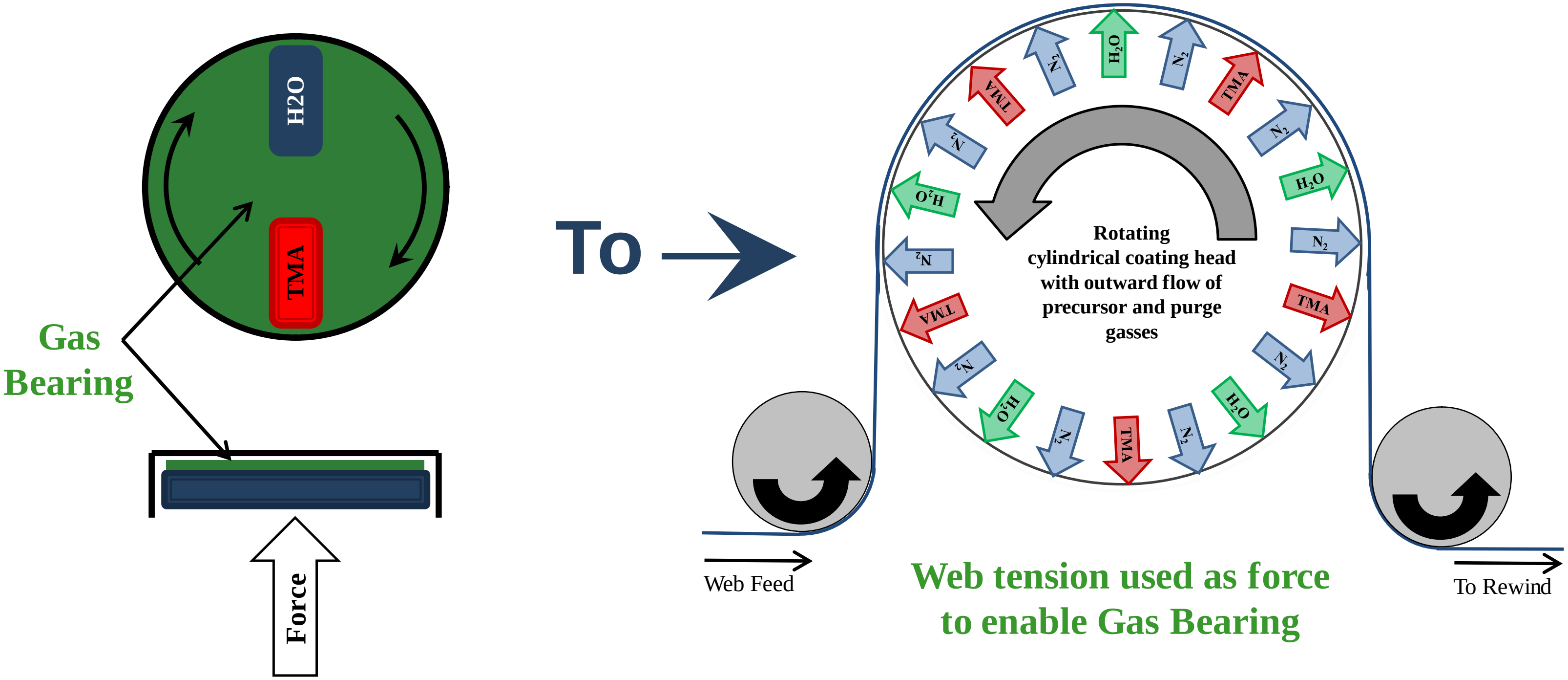
- Kodak, the early pioneer
  - Targeting flexible electronics (semiconductors, gate oxides)
- University of Colorado
  - Characterizing fundamentals of mechanical and process sensitivities
- Cambridge Nanotech
  - Targeting barrier layers for flexible electronics, including barriers

Using a “Gas Bearing” to Control the Gap



- Gas pressure under large area purge regions of the source head counteracts opposing force from opposite side of the substrate
  - Gap defined by balance between gas pressure and opposing force

TNO (Netherlands)

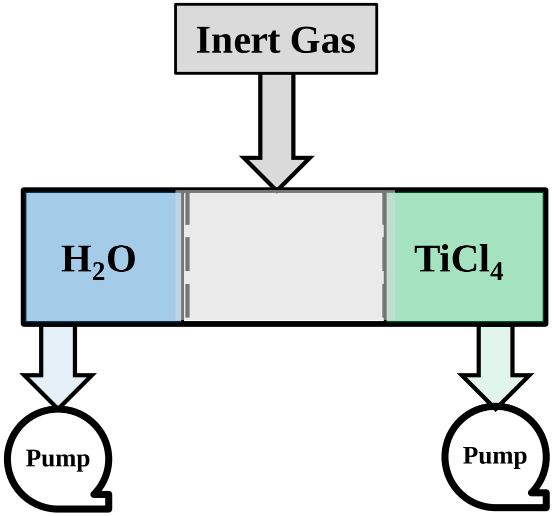


Web tension used as force to enable Gas Bearing

- Prototype rotary disc-based reactor demonstrates very high speed deposition of Al_2O_3 at temperatures > 100C
- Scaling to full R2R @ 300mm width now
  - First depositions reported in presentation at AVS ALD 2012 conference in June

Gas Separation With Vacuum

- Processed under rough vacuum
  - Work to date mostly done at pressure similar to pulse-based ALD at ~ 1 Torr
  - Differential pumping used to create flow away from purge zone

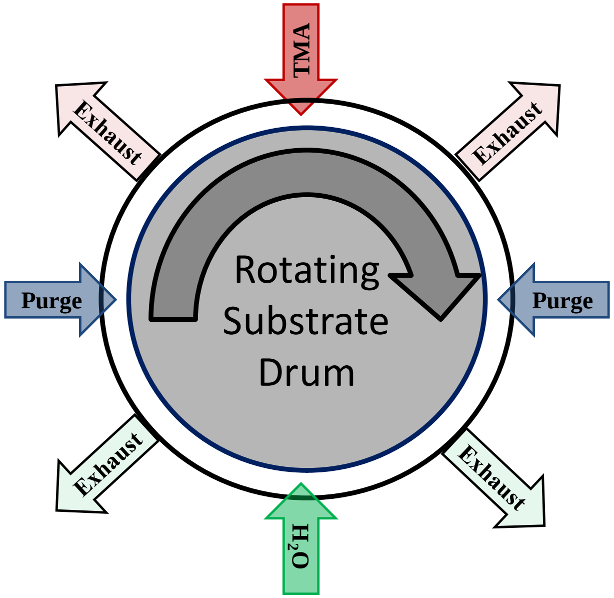


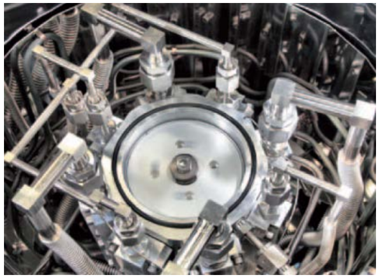
Method allows large gaps in zone separation features

Slots as wide as 1 cm demonstrated

Continuous ALD Processing in Vacuum

Commercially Available

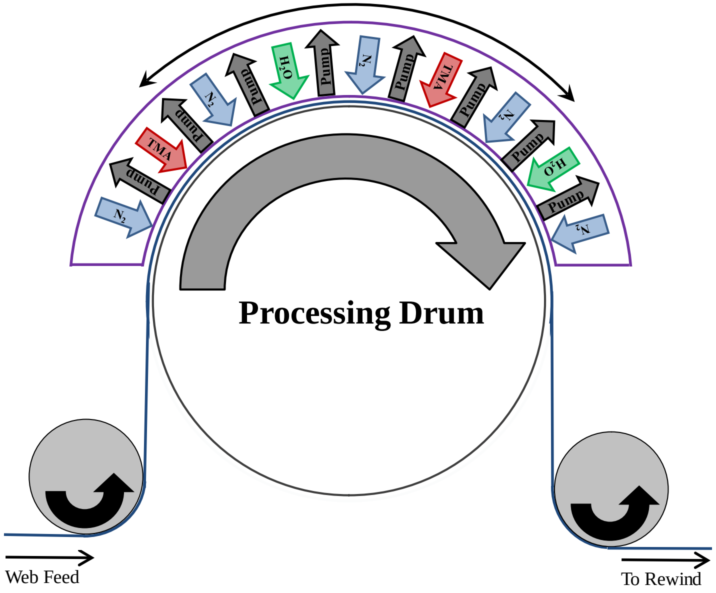




Beneq’s TFS-200R

- Substrate holder is cylindrical, ~120 mm tall by ~100 mm in diameter
- Availability for “Roll to Roll research” announced in 2009
- WVTR < 10^{-3} g/m^2/day for substrate speed of 6 meters/minute
  - 25nm Al2O3

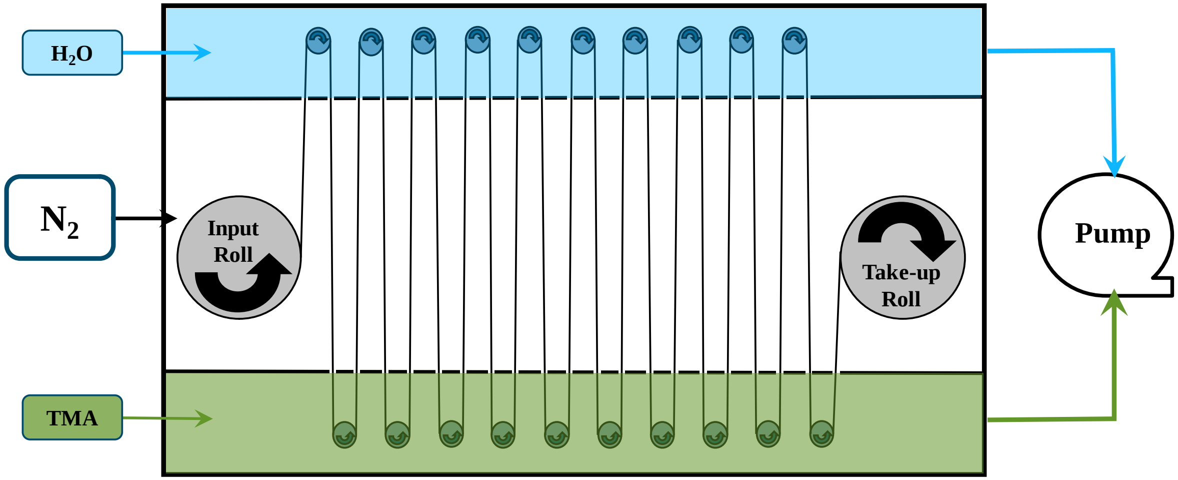
Scaling to Roll to Roll



WCS-500

- Conventional web handling system similar to that used for other R2R systems
- ALD coating head fitted to portion of the drum
  - Oscillation of coating head increases number of cycles deposited in single pass of web
  - Specified to run at speeds up to 2 m/min for 25nm Al_2O_3 coating
- First unit slated for commissioning and delivery to ASTRaL in Q3 of 2012

R2R ALD with Shared Zones



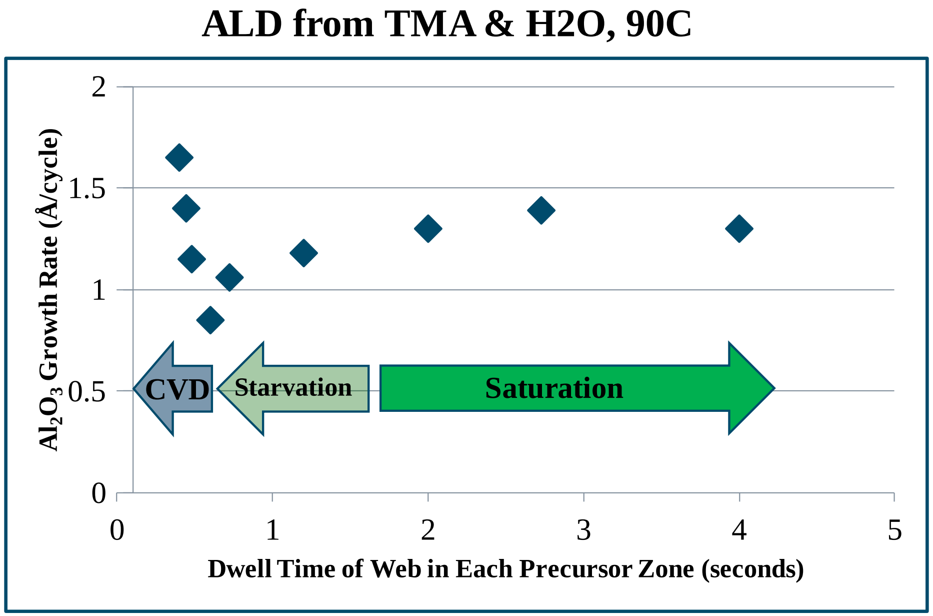
4” Research Reactor

- Web is transported back and forth between precursor zones in serpentine path
- Three total zones in simplest configuration
- Technology under development at Lotus AT
  - Currently targeted toward ultra-barrier films

Scaling Challenges

- Damage to thin ALD layer during rewind
- Web handling in general
  - Precise tolerance required for head to substrate spacing in atmospheric pressure approach
    - Use of gas bearing may help
  - Complicated web manipulation required for serpentine vacuum approach
    - Must prevent contact between coated web surface and guide roller
  - Not a major issue for vacuum approach using a “coating head”
    - Beneq’s system uses conventional web handling incorporated in vacuum sputtering systems, does not require tight tolerances
- ***Water as a precursor at low substrate temperatures***

The Water Speed Limit

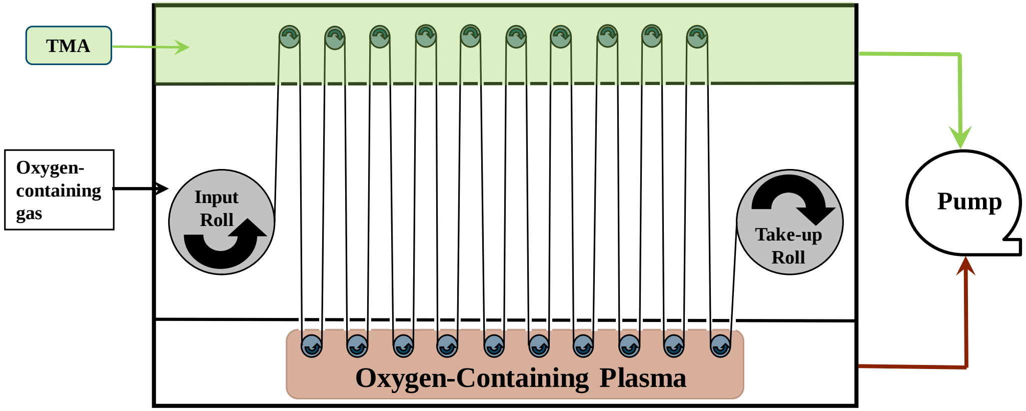


Minimum water concentration required for saturation

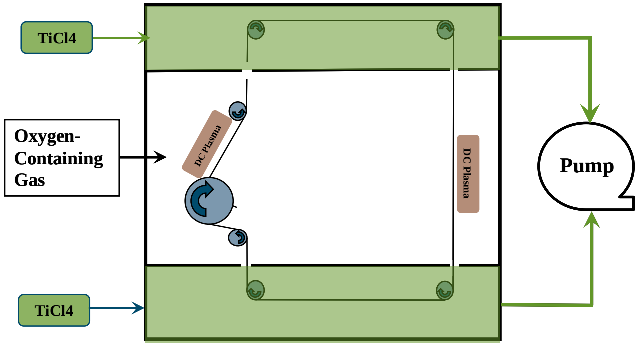
- Excess physisorbed water comes off very slowly at low temperature
  - Long purge time required to preserve film quality, prevent CVD growth
- Problem gets more severe when precursor concentration (dose strength) is higher
  - Overdosing required to achieve conformality, defect “forgiveness”

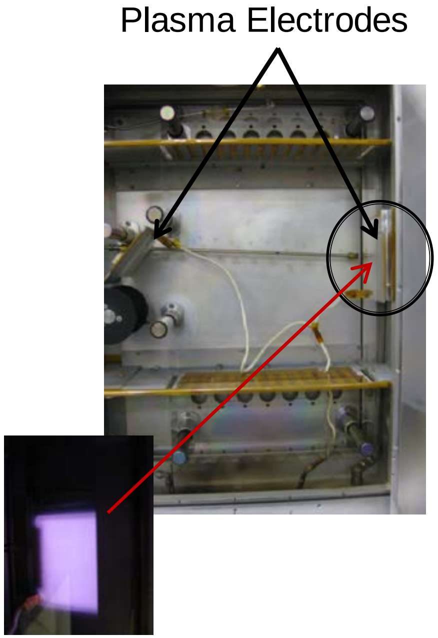
- Depending on temperature, several seconds may be required in purge region of reactor
  - Desorption times of several seconds to one minute required to achieve best barrier results at 100C in pulse-based reactors
- Same phenomenon observed for processes deposited at atmospheric pressure

Substitute Plasma for Water



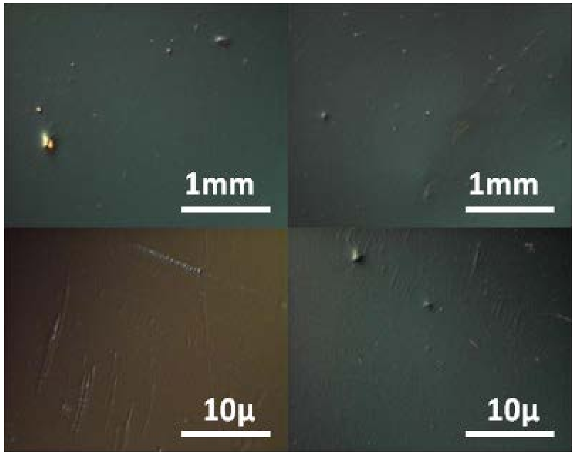
Research Reactor





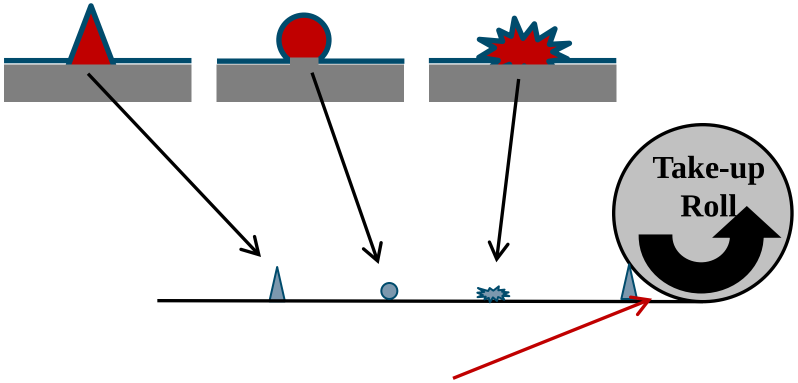
- Use of plasma in place of water eliminates Water Speed Limit
  - Compatible with very low temperatures – even room temperature
- Growth rate per cycle increases
  - 1.5x for Al_2O3, 2x for TiO_2
- Simplifies precursor separation
  - Oxygen half-cycle may be installed in purge zone
    - Doubles number of ALD cycles per pass

Damage to ALD film during Rewind



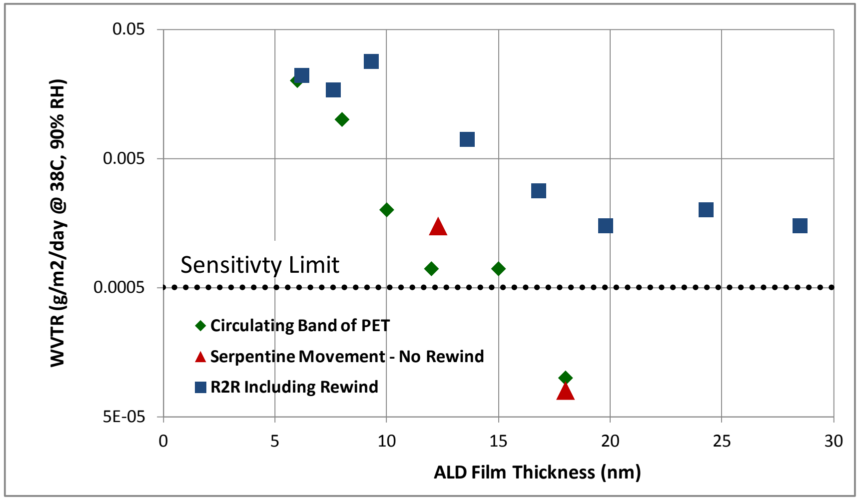
Some polymer substrates can be really challenging!

ALD Films Conformally Coat Defects



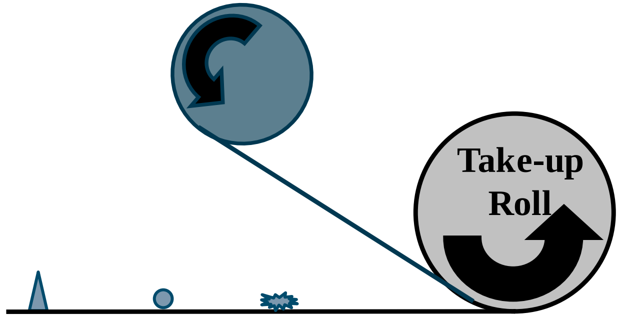
But – Coating over defect can fracture under pressure

- Very thin ceramic film on top of soft polymer is easily damaged
- Coating on raised defects and particles on surface are fractured
- This a problem for all thin film ceramic coatings on polymer



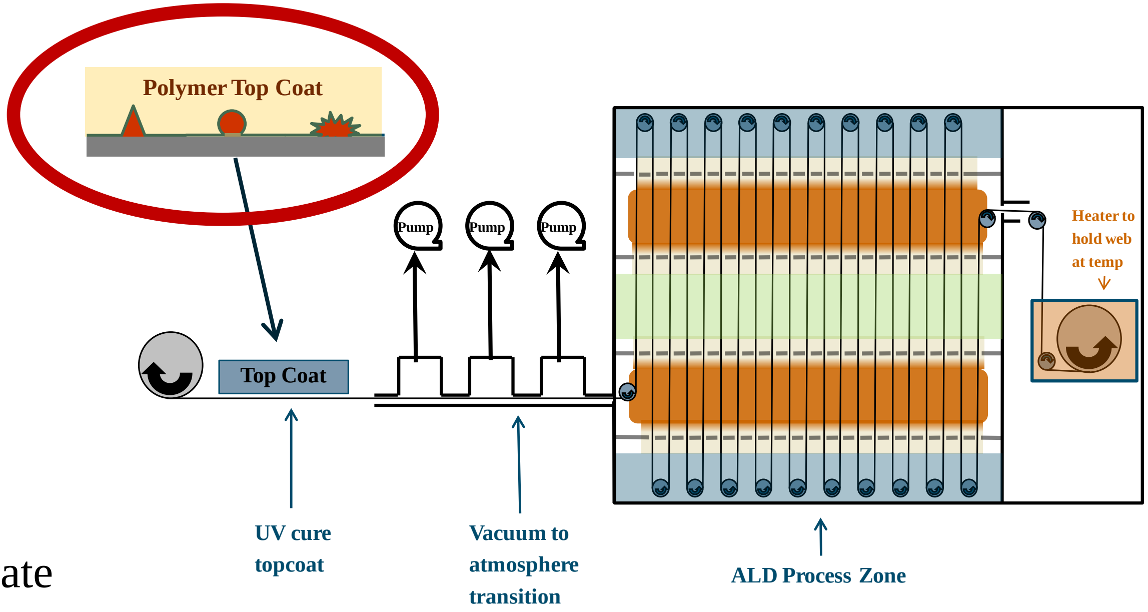
Solutions to Rewind Damage

Some improvement with a simple addition



- Start with smooth, clean substrate material
- Interleave a soft, slippery film during rewind (eg. fluoropolymer)
  - Reduces frequency and magnitude of damaged areas
  - Still susceptible to damage during down-stream processing such as lamination

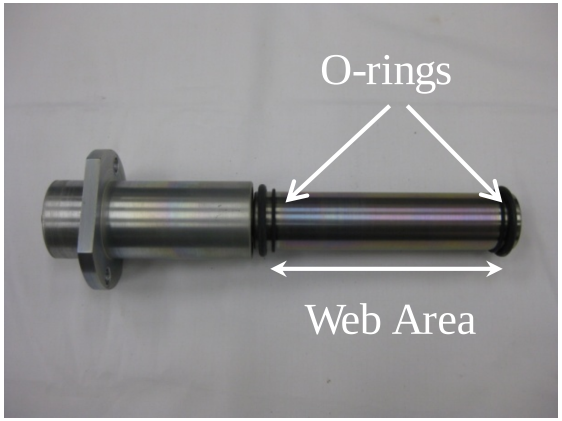
A more robust solution



- New roll of substrate is loaded on spindle at atmosphere
- Web is wound through the system and heated to outgas substrate
  - Held at temperature on internal take-up roll
- ALD Process is applied on the way back out to original roll
  - Wet process topcoat applied prior to rewind

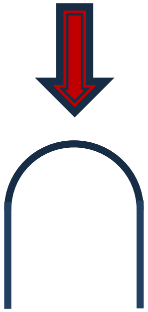
Avoiding Guide Roller Contact

Web Suspension



100mm research reactor uses o-rings at the edges of substrate

Bands used for wider substrates

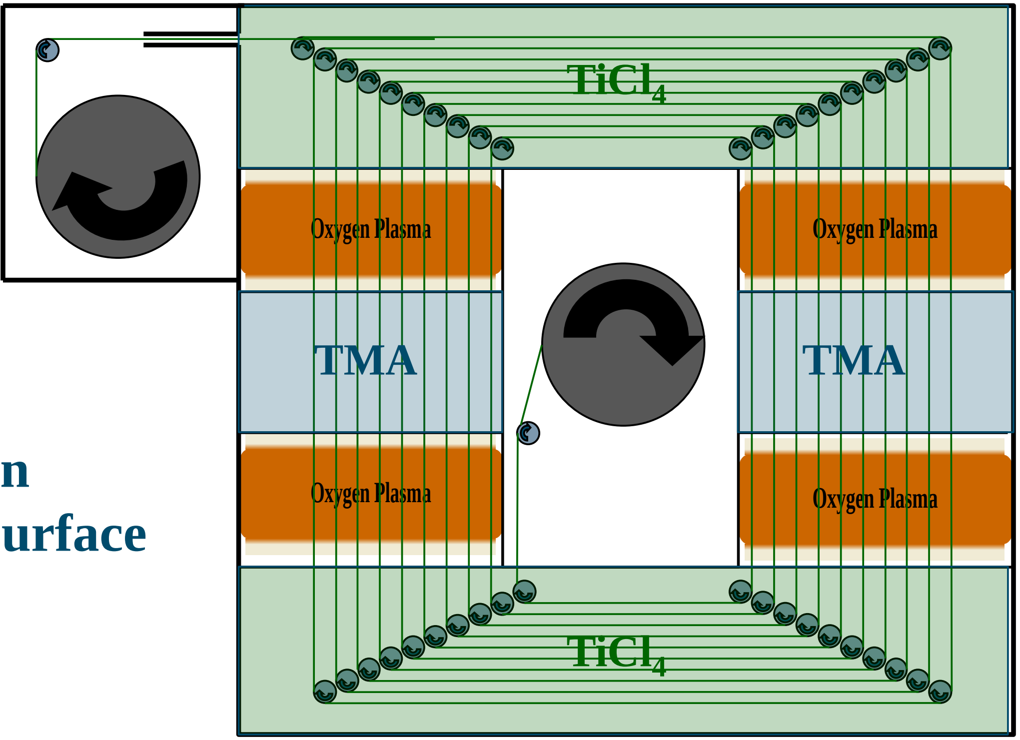


Key to a strong "spine" is to use small diameter rollers. We use 25 to 40mm diameter

- Current method uses raised edges of guide rollers, suspending middle of web away from roller surface
- Suitable for "ultra-barrier" applications
  - Thick substrate material (typically 100-150 µ)
  - Widths up to 1.5 meters

Single-Sided Contact

Concept only



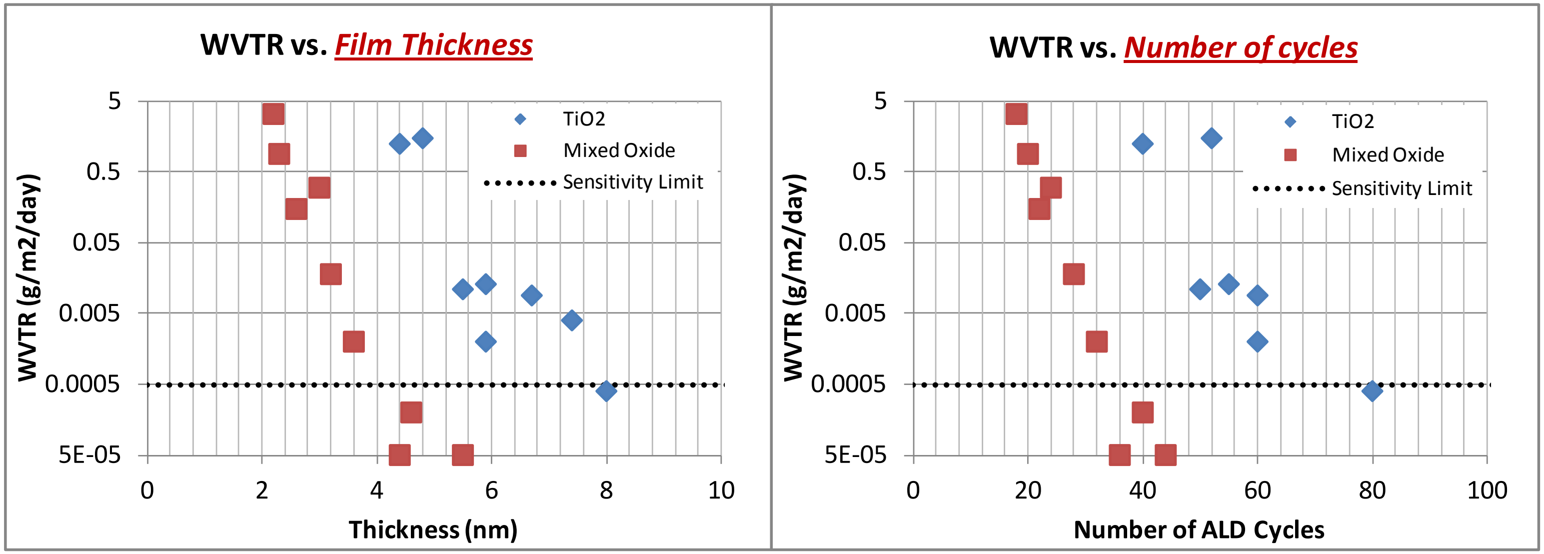
"Stacked" configuration provides 4 ALD cycles per loop of the coil

Coil configuration results in contact only with a single surface of the substrate material

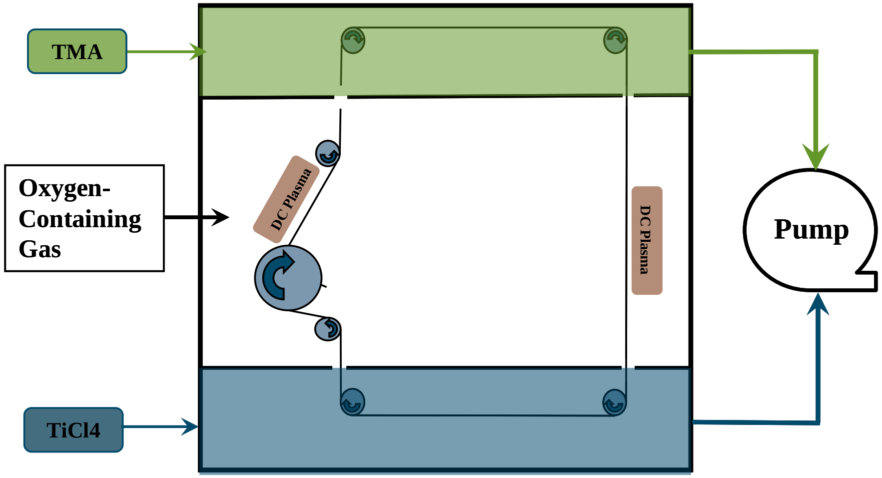
- Suitable for applications requiring thin, wide substrate material, lower film thickness
  - New mixed Al_2O_3/TiO_2 material provides excellent barrier with as few as 30-40 ALD cycles

Barrier Results Using Substrate Translation

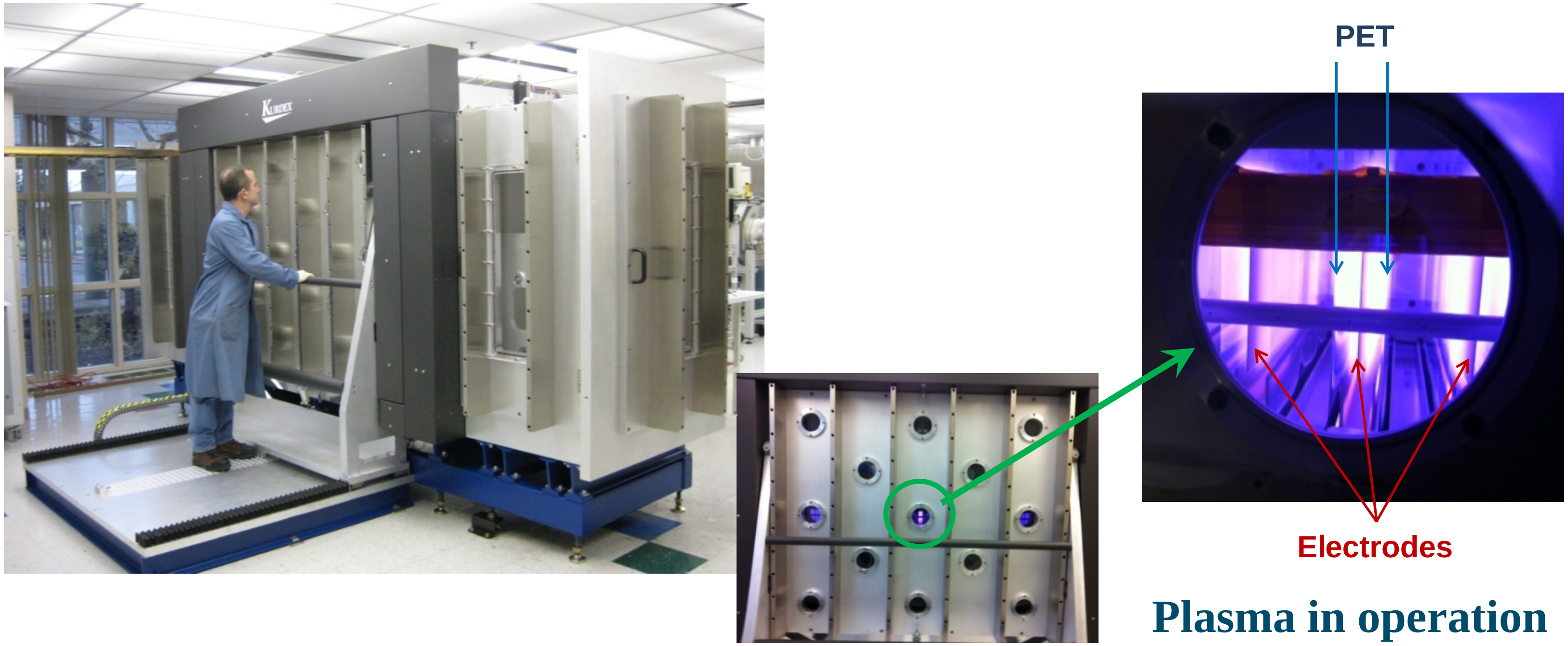
Mixed Oxides



- Single sided coatings on DTF ST-504
- 75C substrate temperature
  - Similar results @ 55C
- Run in "Band Mode" @ 15 m/min speed
  - Speed limited by small plasma electrodes



Scale-up to 300mm Pilot System



Plasma in operation

- 300mm wide substrate material – rolls up to 1200 meters long
- 25 roller pairs in single pass
  - Up to 100 ALD cycles per pass, depending on configuration
- Single sided barriers produced with WVTR below sensitivity limit of MOCON Aquatran (< 5 * 10^{-4} g/m^2/day)
  - ***No rewind***, 6nm mixed oxide film

Status of Commercialization

- ✓ Match or exceed barrier performance demonstrated in pulse-based ALD, using ALD based on substrate translation
- ✓ Overcome speed limit due to water desorption
  - Plasma instead of water
- ✓ Solve issues associated with non-conventional web handling
  - Vacuum based process with coating head can use very conventional equipment
  - Scaled to Pilot level for serpentine configuration
  - Investigating use of gas bearing for atmospheric pressure approach
- ✓ Prevent damage during rewind
  - Solutions identified and tested off-line, but not tested in R2R configuration yet
- ✓ Scale full R2R process to Pilot level
  - Demonstrated using serpentine approach
  - Development underway using atmospheric pressure and vacuum based coating head

This progress in just the last 4 years!

Summary and Outlook

- Research and development of ALD based on substrate translation has increased dramatically in the last four years
  - Several different groups, using several different methods, have demonstrated successful ALD operation
- Several different organizations are scaling up to full roll to roll processing at the pilot scale right now
  - First commercially available equipment shipping this year
  - Ultra-barrier films demonstrated at 300mm scale on web
- Engineering challenges remain prior to full commercialization
  - Film protection during re-wind
  - Web handling optimization
  - Precursor separation for very wide web untested
- Prospects looking good for at least limited scale manufacturing within the next few years
  - Diversity of approaches enhances probability of success