Batch and Roll-to-Roll Atomic Layer Deposition (ALD) processing for ultra-barrier and other applications.

ALF SMITH
CPI is a UK technology innovation centre and the process element of the Government’s High Value Manufacturing Catapult.

We use applied knowledge in science and engineering combined with state of the art facilities to enable our clients to develop, prove, prototype and scale-up the next generation of products and processes.
CPI Printable Electronics is a design, development and prototyping facility for the emerging Printable Electronics (PE) industry.

Funded by :-
- ~33% Catapult (TSB, UK Government)
- ~33% Collaborative Development (UK, EU)
- ~33% Commercial Development (Global)

- Fabrication
- Prototyping
- Access to Scale-able Toolsets
- Commercialisation Support
- Incubator Space

**Facilities**
- 2 clean rooms (Class100 &1000)
- Formulation, optical, & electrical test labs
- 12 incubator offices
- Expert techno-commercial team
WHY TRANSPARENT FLEXIBLE ULTRA-BARRIER?
RIGID ENCAPSULATION

REPLACE GLASS with ULTRA-BARRIER POLYMER FILM

BENEFITS
- FLEXIBLE
- ROBUST
- LIGHTWEIGHT
- THIN
- TRANSPARENCY

ENABLES
- NEW PRODUCT DESIGN
  - COMFORMABLE
  - FLEXIBLE
- R2R LOW COST MANUFACTURING
  - COATING
  - LAMINATING

FLEXIBLE ENCAPSULATION
PRINTABLE ELECTRONICS MARKET

22% ($1.3B) FLEXIBLE

43% ($23B) FLEXIBLE

IDTechEx, 2012
Figure 8. Module life for 2-side cooled (with symbols) and 1-side insulated (dashed) modules.

D.J. Coyle, et al., 2009 34th IEEE, pg. 001943 (2009)
Insufficient moisture barrier on OLED devices
- electrode degradation
- causes dark spots

[Galand, 2010], effect of moisture ingress on OLED device performance. Black spots are caused by oxidation of the cathode
WHAT IS TRANSPARENT FLEXIBLE ULTRA-BARRIER?
### Barrier layer requirements on plastic substrates

<table>
<thead>
<tr>
<th>Material</th>
<th>Water vapour barrier $g.m^{2}.day^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer films</td>
<td>1s-100s</td>
</tr>
<tr>
<td>Food packaging</td>
<td>0.1-10</td>
</tr>
<tr>
<td>Electro-Chromics</td>
<td>0.001-0.05</td>
</tr>
<tr>
<td>Flexible PV</td>
<td>0.000001-0.001</td>
</tr>
<tr>
<td>Flexible OLEDs</td>
<td>0.00000001-0.000001</td>
</tr>
</tbody>
</table>
**Ultra-BARRIER layer requirements on plastic substrates**

<table>
<thead>
<tr>
<th>Application</th>
<th>Moisture Barrier g H₂O/m²/day</th>
<th>Lifetime</th>
<th>UV damage</th>
<th>Flexibility</th>
<th>Cost/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>OLED Display</td>
<td>1 x 10⁻⁶</td>
<td>+5 -10 yrs</td>
<td>X</td>
<td>X ✓</td>
<td>High</td>
</tr>
<tr>
<td>OLED SSL</td>
<td>1 x 10⁻⁶</td>
<td>+10-15 yrs</td>
<td>X</td>
<td>X ✓</td>
<td>Med</td>
</tr>
<tr>
<td>OPV</td>
<td>1 x 10⁻³ - 1 x 10⁻⁵</td>
<td>+25 Yrs</td>
<td>✓</td>
<td>✓</td>
<td>Low</td>
</tr>
<tr>
<td>Inorganic PV</td>
<td>1 x 10⁻² - 1 x 10⁻⁴</td>
<td>+25 Yrs</td>
<td>✓</td>
<td>✓</td>
<td>Low</td>
</tr>
</tbody>
</table>

**Barrier retention over product lifetime!**
Water Vapour Transmission Process

- Pinholes in coating or substrate
- Grain boundaries in coatings – not for amorphous layers
- Defects in substrate
- Debris on surface
- Solution and Diffusion through coating and substrate
- Delamination of coating

Diagram:

- 125um PET
- ? -100 nm barrier
Routes to Ultra-Barrier

1. Single layer – low defect density – near ‘perfect’

2. Multilayer (‘Vitex’ - type)

3. Multi-laminate structures
Single and multi-layer barriers

- A key enabling technology for flexible electronics on plastic

  - Can be the substrate and encapsulation (packaging) for devices
  - ‘Perfect’ layer can provide high barrier (high density, low defects)
  - Multi-layer approach (e.g. Vitex)
Water vapour transmission through barriers of equivalent total thickness

Assumption materials dry from the outset

- H$_2$O (g/m$^2$/day)
  - Low barrier
  - Medium barrier
  - High barrier

- Lag times

Time

Polymer

Single barrier

Double barrier

H$_2$O (g/m$^2$/day)

- see also G. Graff et al, J.Appl. Phys. 2004
Multi-layer Barrier

- Deposition of thin (20 - 50nm) layers of inorganic materials combined with some organic polymeric thin layers
  - Blocks porosity in polymer thin films
  - Dislocates pores providing tortuous path

Barix Multilayers: a Water and Oxygen Barrier for Flexible Organic Electronics
HELIATEK – small molecule evaporated OPV with Multi-layer barrier

ALUMINIUM

ORGANIC

ITO

INORGANIC

POLYMER

INORGANIC

POLYMER

INORGANIC

POLYMER

INORGANIC

POLYMER

200nm

BARRIER

200nm
Multi-layer; ‘VITEX’ Approach

• Multi-inorganic barrier/organic interlayers (multi-DIAD)

• Several players (e.g. 3M, Samsung)

• Cost?

• Robustness in original form?
POLO ULTRA-BARRIER

Fraunhofer (IVV, FEP, ISC)

### Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate material</td>
<td>PET (Melinex 400 CW, 75 μm)</td>
</tr>
<tr>
<td>WVTR</td>
<td></td>
</tr>
<tr>
<td>at 38°C/ 90% r.h. (Aquatan)*</td>
<td>&lt; 5 × 10⁻⁴ g/(m²d)</td>
</tr>
<tr>
<td>at 38°C/ 90% r.h. (HiBarSens®)*</td>
<td>4 × 10⁻⁴ g/(m²d)</td>
</tr>
<tr>
<td>at 38°C/ 90% r.h. (calcium mirror test)</td>
<td>2 × 10⁻⁴ g/(m²d)</td>
</tr>
<tr>
<td>at 23°C/ 50% r.h. (calcium mirror test)</td>
<td>8 × 10⁻⁴ g/(m²d)</td>
</tr>
<tr>
<td>OTR**</td>
<td>&lt; 5 × 10⁻³ cm³/(m²d bar)</td>
</tr>
<tr>
<td>at 23°C/ 0% r.h. (OX-TRAN 2/21)</td>
<td>(below measurement limit)</td>
</tr>
<tr>
<td>VLT*** (spectrum adaptable to application)</td>
<td>82%</td>
</tr>
<tr>
<td>roll width</td>
<td>max. 460 mm</td>
</tr>
<tr>
<td>roll length</td>
<td>max. 500 m</td>
</tr>
</tbody>
</table>

*) The water vapor transmission rate was measured on a large area (≥ 100 cm²) at different positions on the film; **) Oxygen transmission rate; ***) Visual light transmission
Multi-layer/Nanoparticle - Tera Barrier Films, Singapore
GE GRADED ULTRA-BARRIER

Low 10^-5 - Mid 10^-6 g/m2/day (at 23°C 50% RH)
APPLIED MATERIALS

- Barrier with single layer PECVD SiNx silane-based process.
- R2R production
- ~5x 10^-5 g/m²/day @ 20°C/50%RH by Ca Test (300nm on PEN).
- Developing Organic polymer/SiNx diad multi-layer structures

~4x10^-3 g/m²/day
HOLST CENTRE, EINDHOVEN

Barrier Technology:
PECVD SiN/ORGANIC LAYER/PECVD SiN
• DIRECT ENCAPSULATION ON OLED DEVICE
• DAMP HEAT TEST 500hrs, 60C/90%RH, 97% yield for no black spots
• Applying to R2R, Applying to barrier film.

“We have successfully produced over 2.5 kilometers of R2R barrier film based on a single inorganic layer with water vapour transmission rates (WVTR) lower than 10-5 g/m2 per day on commercial-grade PET foil,”

Microwave plasma sources
AEGIS Deposition System
1.4m wide R2R
500,000m²/year
~1-2m/min

Vitriflex has a novel, proprietary barrier film architecture
- Proprietary mixed-oxide material set
- Proprietary thin-film stack based on a “triat” structure
  - Diffusive layer
  - Reactive layer
  - Diffusive layer
- Proprietary hybrid top seal

~1x10⁻⁵ g/m²/day 23C/50% RH
FLEXIBLE GLASS

- Stability
- R2R compatible
- Smoothness

CORNING

ROBUSTNESS!
CPI’s IMMEDIATE INTEREST:

Transparent Ultra-Barrier by Atomic Layer Deposition (ALD)
Batch ALD: $\text{Al}_2\text{O}_3$ using TMA and $\text{H}_2\text{O}$

- Two chemical precursors react in a type of cyclical CVD process
- Reaction is self-limiting and stops at the end of each cycle
- For $\text{Al}_2\text{O}_3$ deposition the precursors are typically:
  - Trimethyl-aluminium (TMA)
  - $\text{H}_2\text{O}$ or $\text{O}_2$ plasma or ozone for oxidation (CPI has all available)
- The 4 steps below constitute 1 cycle for $\text{Al}_2\text{O}_3$ using TMA + $\text{H}_2\text{O}$
Properties of ALD coatings
Because ALD is a surface-mediated gas phase process the films have the following characteristics:

- Highly-conformal – uniform coatings into high aspect-ratio trenches, over step edges and into complex 3D objects
- Low stress – good adhesion; important for MEMS and sensors
- Dense, with few defects – relatively free of pinholes as required for barriers and encapsulation
- Reproducible – ‘digital’ thickness control on sub-nm scale
- Different materials can be combined to form nano-scale laminates
- Deposition can be done at low temperature (even at RT)
- Deposition rates are typically ~0.5-1.5nm/min (process specific)
- Amorphous or partially crystalline films (process specific)
ALD coating of high aspect-ratio features [GENUS]

Highly conformal multilayer films

High-k Dielectrics for DRAM Capacitors
Atomic Layer Deposition (ALD) Batch Coaters

Oxford Instruments
- FlexALTM tool designed for processing semiconductor wafers
- Batch process: coating up to max 200mm wafer 140mm x 140mm

Beneq TFS500
- various internal process chambers
- coating to 370x470mm (GEN 2 size)
- Thermal and plasma (capacitive, to 300mm dia.)
Batch ALD samples produced on polymer films:

• **Extrinsic barrier** (large area measurement)
  MOCON Aquatran 1:  < 5x10^{-4} g/m^2/day

• **Intrinsic barrier** (small area)
  Laser spot Ca Test:  ~1-2 x 10^{-6} g/m^2/day

Excellent reproducibility at AlOx thickness >20nm
Batch ALD planarised PEN substrate

- Barrier possible at <10nm thicknesses in batch
- 15nm thick barrier realised in R2R, <5x10^{-4} g/m^2/day @ 0.4m/min

Mocon measurements on ALD barriers

Detection Limit
Aquatran 1
Sample 10 x 10 cm² measured area 50 cm²

WVTR [g/m²/day]

1.0E-02

1.0E-03

1.0E-04

Early barrier samples

With better handling and chamber conditioning

Sequence of samples

Mocon: lower sensitivity limit

With better handling and chamber conditioning
Barrier layer benefits of ALD

- high barrier performance with no lag time
- intrinsic WVTR @ $\sim 1 \times 10^{-6}$ g/m²/day
- amorphous high density barrier layers
- low materials usage and costs

- key issue is to overcome defects (particles)
CALIBRATED Ring-down laser absorption

Single ALD layer, Batch production

Best values:
2 x 10^{-5} g/m^2/day
@ 26°C, 80%RH

76 cm^2 sample area

4 x 10^{-5} g/m^2/day
@ 35°C, 90%RH

Lowest detectivity
2 x 10^{-5} g/m^2/day
DH degradation of monolithically integrated CIGS submodules on glass substrates (10x10 cm²) - ~15% eff.

LS = Light soak recovery

DH 80C, 80%RH
DH degradation of monolithically integrated CIGS submodules on glass substrates (10x10 cm²) - ~15% eff.

Encapsulations (E=Epoxy; ALD= AlOx)
R2R ALD – Spatial ALD
R2R Spatial ALD
Examples
- Levitech
- Solay Tech
- Beneq
- TNO/VDL Flow
++++

REVIEW PAPER:
P. Poodt, D. Cameron, E. Dickey, S.M. George, V. Kuznetsov, G.N. Parsons, F. Roozeboom, G. Sundaram, A. Vermeer, JVST-A 30 (2012) 10802

Example: TNO
Homogeneous deposition of Al2O3: layer thickness of ~23 nm at 0.5 m/min web speed and 0.5 Hz drum rotation
**Serpentine web translation**, single-sided coating
300 mm wide web, up to 600 meters long
25 roller pairs: up to 100 ALD cycles in a single-pass
Suitable for web widths < 1.5 meters and thickness > 100 μm
Produced 6 nm barrier film @ 30 m/min with WVTR < 5 x 10^-4 g/(m2·d)

**COIL REACTOR** – concept only
Single-sided web contact only: well-suited for widths > 1.5 m, thickness < 100 μm
Each lap = 4 complete ALD cycles
7 laps @ 300 m/min → ~5 nm ALD film thickness → ~0.005 g/(m2·d) WVTR
Cost estimate $0.03/m2
Collaboration between hardware and process development companies.

- Excellent prospects to scaling to +1 meter widths, due to reasonable mechanical tolerances
  - 0.5 mm gap across 500 mm web width
- Second generation systems built.
- Collaboration with the Centre for Process Innovation (UK)
  - Facilitates rapid technology engagement with industry
  - CPI will collaborate with institutes and companies Globally for wide range application for R2R ALD.
- Roadmap for R2R ALD
  - Scaling beyond 500 mm, line-integration
  - Further web speed improvement by PEALD
  - Pre-and post-processes to address particles

Now Operational at CPI
CPI R2R ALD development

Key focus for R2R ALD development:

• production line speeds of >1 m/min
• small machine footprint
• web width 0.5m
• thin high density barrier layers
• methods to reduce defects + effect of defects
• robust mechanical barrier materials
• low production cost
CPI R2R ALD system.
R2R ALD deposition.
  • TMA + Water process
  • Substrate metallised PET
R2R-ALD PROCESS PERFORMANCE

• Process tuning phase

• Short rolls of barrier produced

• Early stage barrier performance promising
  15 – 40nm thick AlOx on 125 micron thick PET+PEN has shown extrinsic barrier:
  \(< 5 \times 10^{-4} \text{g/m}^2/\text{day} \ (\text{Mocon Aquatran 1})\)

• Shown at 0.1, 0.2 and 0.4 m/min (40, 20, 15nm thick)

• Substrate temperature 105°C

• Extensive measurements underway
R2R ALD barrier demonstration

- Coated using WCS 500 (R2R ALD pilot).....operated at LUT Univ. Finland
- Substrate is Dupont Teijin OPTIFINE PEN (125 µm)
- 20 nm thick Al₂O₃, from TMA + H₂O
- Process temperature 105 C
- Coating width 500 mm, samples cut out to 120 x 120 mm
Optical calcium test device

- Characterization courtesy to L. Moro & Z. Zeng (S. Cheil Industries)
- Temporary barrier is not good barrier under 85°C / 85% relative humidity conditions
- Barrier foil sample not large enough to cover full Ca test device area -> permation from sides taking place, only A and B areas considered for WVTR

Ca test results

- No clear pin-hole generation or growth observed
- WVTR ~5.0E-6 g/m2/day at 20C/50%RH is estimated
- Ca test stopped after 800hrs at 85C/85%RH due to edge penetration, but the barrier itself is still good
- Samples also measured with MOCON Aquatran 1, repeated measurements
  <5*10-4 g/(m2 day) at 40 C / 90 % RH
FUTURE

**Ultra-barrier Targets**

- Line speed >5m/min
- Barrier $1 \times 10^{-6} \text{ g/m}^2\text{/day}$
- Barrier coating cost <$10/m^2$

**Other coatings**

- as direct encapsulation (OLED, PV, PE, SENSORS)
- as Nano-laminates (new materials)
- as ‘perfect’ interfaces
- as Contacts (work function control)
- as Gate dielectrics
- TFT devices
- PV structures
- Surface active coatings.
- Smart Coatings
R2R -CIGS

CPI member of FP7 large project R2R-CIGS

Partners:
TNO (NL), EMPA (CH), FLISOM (CH), ZSW (DE), ISOVOLTAIC (AU), MANZ (DE), BENEQ (FI), SOLAY-TEC (NL), MONDRAGON (ES)

Full R2R pilot production line for flexible CIGS solar cells
Clear Barrier Foil for thin film CIGS flexible PV
Direct encapsulation of thin film CIGS flexible PV
The NanoMend project has received funding from the European Community’s Seventh Framework Program (FP7/2007-2013) UNDER Grant Agreement No. 280581
HIBPE – Innovate UK project

CPI, Sedgefield
CAMVAC Ltd., Thetford
G24 Power Ltd., Newport
Inside 2 Outside Ltd. (I2O), Cambs
Tata Steel UK
SPECIFIC, Swansea
Conclusion

1. Many promising Ultra-barrier technologies
2. ALD technology has high potential for Ultra-barrier applications
3. R2R ALD possible
4. Other applications for ALD and R2R ALD insight

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