Vacuum deposition of high performance gas barrier materials for electronics applications

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Barrier layers for electronics

- Component lifetime
- Tolerance
- Mechanical properties
- Process speed (cost)
- Transparency

10^0 10^-1 10^-2 10^-3 10^-4 10^-5 10^-6 WVTR

OLEDs
Excitonic PVs
DSSC
Vacuum insulation panels
OTFT
Pharmaceuticals
Food packaging
Barrier layer defects

If permeation dominated by ‘large’ defects

WVTR dependent on defect area

Activation energy of permeation that of substrate
Multilayer films

- ‘Lag time’ for water to penetrate each layer of a barrier film dependent on:
  - Layer thickness
  - Diffusivity

- Multiple layers with a low defect density:
  - Permeation more dominated by diffusion through nanodefects
  - Larger effective ceramic layer thickness
  - Very long time to reach equilibrium permeation
  - No build-up of residual stress
  - Impact on mechanical properties?
Design of high barriers

- Decrease (effective) density of macrodefects
  - Smooth substrate
  - Processing control
  - Multiple layers

- Extend time before equilibrium permeation
  - Thick (multiple) layers
  - Decrease diffusivity

- At equilibrium
  - Decrease diffusivity & solubility
    - Dense coating
    - Chemistry
Oxford Web Coater: Exterior

- Single, cooled, deposition drum
- Film width = 350mm, Thickness 7 to 250μm
- Web speed up to 300m/min
Oxford Web Coater: Deposition

- Plasma treater
- Dual magnetron sputtering or thermal evaporation
- Polymer coating by flash evaporation and electron beam cure
Objective

- Deposition of acrylate and Al$_2$O$_3$ onto PEN for gas barrier applications
- Aiming at very high barrier levels by combination of:
  - High quality polymer substrate
  - Dense Al$_2$O$_3$ layer(s)
  - Flash-evaporated acrylate layer(s) for smoothing and separation of any multiple layers.
Acrylate coating

TRPGDA onto PENQ65, 50 m/min drum speed, e-beam current 400mA

ATR-FTIR

ATR:
Ge crystal (n= 4), angle 45°
PEN polymer (n=1.77, x axis)

\[
d_p = \frac{10000}{\omega 2\pi n_{Ge} (\sin^2 \theta - n_{PEN}^2)^{1/2}}
\]

\[
d_p = 0.66 \mu m \text{ (at } 1000 \text{ cm}^{-1})
\]

no trace of PEN absorption: \(d_{\text{acrylate}} > d_p\)
good qualitative agreement between acrylate depositions performed on PEN and Si substrate
Acrylate coating

- FTIR can also be used to determine curing of acrylate
- With a lower e-beam current (red spectrum)
  - ratio of CH bending and stretching band intensities (1000-1200 and 2900-3000 cm\(^{-1}\), respectively) is different
  - carboxylic group appears at different frequency.
- Compare with spectrum of a partially-cured acrylate layer (Affinito, TSF 308, 19, 1997): decrease in e-beam current has indeed caused a partial curing of the polymer layer (see inset).
Acrylate coating

- Acrylate thickness determined by means of step profiler (on Si) and spectroscopic ellipsometry (on Si and PEN)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silicon (SE)</th>
<th>PEN (SE)</th>
<th>Silicon (profilometer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.7 µm</td>
<td>-</td>
<td>9.8-11.5 µm</td>
</tr>
<tr>
<td>2</td>
<td>58 nm</td>
<td>-</td>
<td>45 nm</td>
</tr>
<tr>
<td>3</td>
<td>15.2 µm</td>
<td>15.5-17.5 µm</td>
<td>16.1-17.5 µm</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>14.9-15.3 µm</td>
<td>-</td>
</tr>
</tbody>
</table>

Pseudo-dielectric function of 58 nm thick acrylate layer on Si
At \( \lambda = 633 \text{ nm} \): \( n = 1.503; \ k = 0.0044 \)

Pseudo-dielectric function of 15.3 µm thick acrylate layer on PEN
At \( \lambda = 633 \text{ nm} \): \( n = 1.498; \ k = 0.0024 \)
Acrylate coating

- Confocal microscopy of surface topography

- PEN Q65 surface
  Only irregularities at the nm scale – high quality surface

- Acrylate coating surface
  Significant smoothing (occasional 100nm protrusions in some cases – maybe ‘snow’?)
Al\textsubscript{2}O\textsubscript{3} deposition

- Reactive magnetron sputtering
- 50m/min, 1.92kW-2.4kW
- Multiple rotations to build up thick AlO\textsubscript{x} layer
- Various \textit{O\textsubscript{2}/Ar} mixes
  - 5 sccm \textit{O\textsubscript{2}/95 sccm Ar}
  - 20 sccm \textit{O\textsubscript{2}/200 sccm Ar}
poisoned target
- voltages approx 300 V
- very low sputtering rate (2.7 nm/min)
- poor WVTR 1-1.3 g/m²/day, independent of film thickness

metal target
- voltages > 500 V
- high sputtering rate (17.5 nm/min)
- very good WVTR <10⁻³ g/m²/day
Reactive sputtering

Deposition of from metal target leads to low defect/higher density coatings

Our system allows for:
- oxidation during sputtering
- post-deposition oxidation in chamber

Activation energy depends on oxidation conditions/layer thickness
Al₂O₃ deposition

Chemical analysis: FTIR

- Symmetric band centered at 700 cm⁻¹
  Al-O and O-Al-O stretching mode.
- Any OH functionalities are not observable within the noise due to H₂O absorption (3200-3600 cm⁻¹)

<table>
<thead>
<tr>
<th>wavelength range [cm⁻¹]</th>
<th>bond</th>
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<tbody>
<tr>
<td>590-700</td>
<td>O-C=O bending</td>
</tr>
<tr>
<td>650-700</td>
<td>O-Al-O bending</td>
</tr>
<tr>
<td>750-850</td>
<td>Al-O stretching</td>
</tr>
<tr>
<td>1000-1200</td>
<td>Al-CH₃ stretching</td>
</tr>
<tr>
<td>1500-1700</td>
<td>AlC=O stretching or Al-COOH</td>
</tr>
<tr>
<td>2600-3800</td>
<td>O-H stretching</td>
</tr>
</tbody>
</table>

Kim et al., TSF 237 (1994), 57
Al₂O₃ deposition

Spectroscopic ellipsometry

- High refractive index
  - not strongly dependent on film thickness for thick films or on deposition regime
- Tail in UV region and high \( n \) may suggest incorporation of up to 10% AlN.
Al$_2$O$_3$ deposition

Chemical analysis: XPS

Film surface stoichiometry: AlO$_{1.9}$C$_{0.9}$
- BE values in agreement with literature: BE$_{\text{Al}}$ = 74.0 eV, BE$_{\text{O}}$ = 531.0 eV
- oxygen-rich film: surface effect due to oxidation
- carbon contamination (C up to 20% without pre-sputtering, also observed in XPS measurements of other Al$_2$O$_3$ layers).
- No nitrogen observed
Deposition of acrylate and Al$_2$O$_3$ layers after exposure of the acrylate layer to air. Original thickness of acrylate: 15µm

- Decrease of the acrylate layer thickness during Al$_2$O$_3$ film deposition:
  - O$_2$ plasma etching of the acrylate?
- Potential important consequences in engineering the multi-layer.
Effect of acrylate

- Confocal microscopy of surface topography

With acrylate (deposited in-line with $\text{Al}_2\text{O}_3$)

Without acrylate

<table>
<thead>
<tr>
<th>Image number</th>
<th>10nm peaks</th>
<th>100nm peaks</th>
<th>Pinholes up to 15nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
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<tr>
<td>5</td>
<td>16</td>
<td>5</td>
<td>1</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Image number</th>
<th>10nm peaks</th>
<th>100nm peaks</th>
<th>Pinholes up to 20nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Many</td>
<td>19</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Many</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>Many</td>
<td>14</td>
<td>2</td>
</tr>
</tbody>
</table>
Conclusions

- Very high barrier ($\sim 10^{-3}$ g/m$^2$.day WVTR) achieved with single layer Al$_2$O$_3$
- Two regimes of Al$_2$O$_3$ deposition
- Acrylate smooths the surface of the substrate and leads to a more defect-free Al$_2$O$_3$ if deposited in-line