Optimization of Bond Strength & Barrier Performance for Ultra-High Web Speed Metallizing Applications

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Outline

Introduction & Megatrends

Thin Film Mechanics on Packaging Substrate Materials

Bond Strength

Nexus-E Surface Modification Technology

Nexus-E Process Performance on PET, PP’s & PE

Summary
World’s #1 semiconductor and display equipment company

- AMAT stock listing on NASDAQ
- $14.5 billion revenue
- $1.8 billion R&D spending
- >11,900 patents
- Headquartered in California’s Silicon Valley
- ~18,400 employees
- 90 locations in 17 countries
R2R COATING SYSTEMS

TOPMET & TOPCOIL
Barrier coatings for food packaging and other advanced industrial coatings.

TOPBEAM
Special barrier & optical coatings used in transparent packaging & anti-counterfeit films.

SMARTWEB
Market leader in ITO deposition for projective capacitive touch panel manufacturing.

PECVD Tool
R2R solution for deposition of dielectrics, ultra high barriers and semiconductor materials for display.
AMAT R2R Evaporation Tool Evolution

From 1953
- R2R Drum Metallizer
- Basic Al Process

From 1983
- Electron Beam Evap.
- R&D & HVM Tools
- Metal Oxides

From 1993
- TopMet Platform
- HVM Metallizer
- Basic Al Process
- Plasma Pre-Treatment

From 2010
- TopMet Clear Platform
- Reactive & Plasma AlOx
- Advanced Film Winding

October 2018
NEXUS-E

LEAD BY INNOVATION AND CLIENT BASE

15 Number of Bond Strength Patents
>150 Number of R2R Granted Patents
>730 Number of R2R Coaters installed

NUMBER OF PATENTS
>150
>730

NUMBER OF COATERS INSTALLED
Megatrends In Vacuum Processed Packaging Industry

- Emergence of eco-friendly products
  - Sustainable & re-cyclable packaging

- Changing brand awareness
  - Cultural westernization

- Brands leveraging value chain to reduce cost
  - Harmonizing packaging formats & material standards

- Accelerated evolution of requirements
  - Shelf life, new materials, form factor, downgauging whilst retaining same touch & feel

- Improving product quality & yield
  - Tight cooperation between customers & tool makers
**Concept of Fracture, Delamination & Bond Strength**

- **Fracture**: Rapid, unstable growth of cracks resulting in mechanical failure.
- **Crack Growth**: Occurs when sufficient mechanical energy is supplied to overcome energy of creation of new crack surface.
- **Delamination**: Along the length of the interface between the substrate & the deposited layer.

### Mechanical bond strength
- Controlled by specific material properties:
  - Lattice match between layer & substrate
  - Interfacial bond energy

### Bond Strength Table

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Length (Å)</th>
<th>Bond Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>1.54</td>
<td>409</td>
</tr>
<tr>
<td>C-Al</td>
<td>2.24</td>
<td>255</td>
</tr>
<tr>
<td>C-O</td>
<td>1.43</td>
<td>1076</td>
</tr>
<tr>
<td>Al-Al</td>
<td>3.00</td>
<td>186</td>
</tr>
<tr>
<td>Al-O</td>
<td>1.92</td>
<td>512</td>
</tr>
</tbody>
</table>
Bond Strength Testing

PEEL STRENGTH MEASUREMENT

- Semi-quantitative description of layer adhesion strength → repeatable & reliable
- **EMA method preferred** due to more robust sealing step & increased number of replicates for statistical verification

<table>
<thead>
<tr>
<th></th>
<th>AIMCAL</th>
<th>EMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sealing Size</td>
<td>1 x 3 in = 25x76 mm</td>
<td>20 x 40mm</td>
</tr>
<tr>
<td>Sample Width After Sealing/Cutting</td>
<td>1 in = 25 mm</td>
<td>15 mm</td>
</tr>
<tr>
<td>RH</td>
<td>50 %</td>
<td>50 %</td>
</tr>
<tr>
<td>Storage Temperature</td>
<td>22.2°C (72°F)</td>
<td>23°C</td>
</tr>
<tr>
<td>Sealing Temperature</td>
<td>104.4°C (220°F)</td>
<td>105°C</td>
</tr>
<tr>
<td>Sealing Pressure</td>
<td>15 psi = 1.03 bar</td>
<td>4 bar</td>
</tr>
<tr>
<td>Sealing Time</td>
<td>15 sec</td>
<td>20 sec</td>
</tr>
<tr>
<td>Peel of Angle</td>
<td>180°</td>
<td>180°</td>
</tr>
<tr>
<td>Peel Velocity</td>
<td>12 in/min = 304.8mm/min</td>
<td>50 mm/min</td>
</tr>
<tr>
<td>No. of Replicates</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Result</td>
<td>N/in</td>
<td>N/15mm</td>
</tr>
</tbody>
</table>

PITFALLS IN BOND STRENGTH TESTING

- Peel angle impacts peel test performance
- High peel speeds result in increased data scatter
- Impact of sealant film thickness
- Impact of sealing time, temperature and pressure

Improved Accuracy & Repeatability
Bond Strength Improvement Technology

**TECHNOLOGY**
- Inline pretreatment required to enhance adhesion of inorganic layer stacks on polymeric substrate materials
- DC Glow discharge source typically used

**BENEFITS**
- Surface water release
- Increases reactivity of polymer surface
- Improves film adhesion, film density, barrier performance, optical and electrical performances

**LIMITATION**
- High web speed = limited residence time for substrate in pretreatment source
- Low ion current density & activated neutral concentration = limited pretreatment effect

**SOLUTION**
- High charged species density Nexus E Power technology
- Metallized layer protection through use of Nexus E Flow technology

Diagram:
- Oxygen ion
- Oxygen radical
- Free binding
- Radiation
- Electron
- Plastics
Pretreatment Technology

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Pretreatment Technology

**TECHNOLOGY**
- Plasma pretreatment required to enhance adhesion of inorganic layer stacks on polymeric substrate materials
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**SOLUTION**
1. High charged species density Nexus E Power technology
2. Metallized layer protection through use of Nexus E Flow technology
NEW! Nexus E-Power Surface Treatment

Nexus E-Power Pretreatment Delivers

Optimum charged species energy & dose

Combinatorial charged species delivery system, compatible with a wide range of process chemistries and substrate materials without compromising web speed

Nexus E-Power Features

Improved cooling efficiency
Automatic process control
Simultaneous improvement in winding performance for thin, low $T_g$ substrate materials
How Does Nexus-E Power Work?

- Incident high energy species penetrates surface
- “Thermal spike” breaks chemical bonds at depth controlled by species energy
- Charged particle dose ↑ - Bond cleavage density ↑

Nexus E-Power Influence

<table>
<thead>
<tr>
<th>Layer Description</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidized layer (0-1 nm)</td>
<td><img src="image" alt="Oxidized layer" /></td>
</tr>
<tr>
<td>Carbonized layer (1-100 nm)</td>
<td><img src="image" alt="Carbonized layer" /></td>
</tr>
<tr>
<td>Crosslinked layer (100-1500 nm)</td>
<td><img src="image" alt="Crosslinked layer" /></td>
</tr>
<tr>
<td>Unchanged layer (&gt;1500 nm)</td>
<td><img src="image" alt="Unchanged layer" /></td>
</tr>
</tbody>
</table>

Traditional plasma pre-treatment depth < 5 nm!
Impact of Charged Species Dose on Chemical Bonding

Surface modification observed via XPS

<table>
<thead>
<tr>
<th>ID</th>
<th>Proportion of Carbon Compounds Obtained After Peak Deconvolution</th>
<th>Contact Angle</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₂ (~ 285 eV)</td>
<td>γ ~ 40 mN/m</td>
<td>γ &gt; 56 mN/m</td>
</tr>
<tr>
<td>Raw PET</td>
<td>63.9%</td>
<td>~ 66°</td>
<td>~ 26°</td>
</tr>
<tr>
<td>Nexus-E Power</td>
<td>56.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-O &amp; C-N (~ 286 eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.6%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₂ (~ 288 eV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R-C=O (~ 288 eV)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

% Change in surface concentration proportional to ion dose

7% decrease in surface concentration

7% increase in surface concentration

Nexus-E Power

More Hydrophilic

γ ~ 40 mN/m
Contact Angle ~ 66°

γ > 56 mN/m
Contact Angle ~ 26°
No Change in Surface Roughness

- Optimum charged species dose **does not** result in an increase in surface roughness
  - Primary structural changes are sub-surface in nature only
    - Increase in substrate disorder & fluorescence measured with Raman but without significant increase of D&G bands
    - Weak increase in optical color ($b^*$) in transmission indicative of sub-surface disorder & graphitization only

Untreated Substrate  
Nexus E Treated Substrate
NEW! Nexus E-Flow Metallized Layer Protection

Both sides of the Al layer protected

- **Top layer**: reduces metal pickup during roller contact
- **Bottom layer**: anchors substrate to deposited layer
- **Indirect benefit**: higher surface energy interface between substrate & metallized Al layer

Nexus-E Flow enables $\text{AlO}_x$ like bond strengths for metallized Al layers
Impact of Nexus-E Flow on Defectivity

<table>
<thead>
<tr>
<th></th>
<th>No Nexus-E Flow</th>
<th>With Nexus-E Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinhole count</td>
<td>41</td>
<td>4</td>
</tr>
<tr>
<td>Pinhole mean dimension (μm)</td>
<td>12.5</td>
<td>14.5</td>
</tr>
<tr>
<td>WVTR (g/m²/day)</td>
<td>0.56</td>
<td>0.31</td>
</tr>
<tr>
<td>OTR (cm³/m²/day)</td>
<td>0.53</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Reduction in pinhole count and WVTR, following implementation of reactive pre & post-treatment solution for 2.2 OD Al layer deposited on 12 μm thick PET

Nexus-E Flow safely “packages“ sensitive Al layer reducing the risk of metal pickup

Up to 10X reduction

Up to 45% reduction
How Does Nexus-E Flow Work?

Pseudo-epitaxial buffer layer reducing interfacial strain

- Improved lattice match to substrate
- Increased density of strong chemical bonds to substrate
- Reduced risk of crack generation & propagation at interface

Nexus-E Flow initial AlO$_x$ layer provides effective route to increasing bond energy by > 2x
### Impact on Bond Strength

#### Energetic Species Bombardment
- Presence of chemical treatment & skin layer can be accounted for

#### AlOx Seed Layer
- Control algorithm used to automatically adjust Nexus-E Power & Nexus-E Flow
- Partial metal removal only with parallel EAA sealant cohesive failure

#### Table: Adhesion Without/With Nexus-E (N/15 mm)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Thickness (µm)</th>
<th>O.D. (a.u.)</th>
<th>Adhesion Without Nexus-E (N/15 mm)</th>
<th>Adhesion With Nexus-E (N/15 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>12</td>
<td>2.2</td>
<td>2.5</td>
<td>5.8</td>
</tr>
<tr>
<td>BOPP</td>
<td>18</td>
<td>2.2</td>
<td>0.9</td>
<td>3.9</td>
</tr>
<tr>
<td>CPP</td>
<td>25</td>
<td>2.2</td>
<td>0.7</td>
<td>3.6</td>
</tr>
<tr>
<td>PE</td>
<td>30</td>
<td>2.2</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Impact on Water Barrier

~2-3x BETTER WVTR PERFORMANCE LEVELS

Impact on Al nucleation & growth mode particularly on polyolefins
Transition from 3D/island growth mode to layer by layer growth mode
Dense continuous layers deposited at lower thicknesses

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Thickness (µm)</th>
<th>O.D. (a.u.)</th>
<th>WVTR Without Nexus-E (g/m²/day)</th>
<th>WVTR With Nexus-E (g/m²/day)</th>
</tr>
</thead>
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<tr>
<td>PET</td>
<td>12</td>
<td>2.2</td>
<td>0.56</td>
<td>0.31</td>
</tr>
<tr>
<td>BOPP</td>
<td>18</td>
<td>2.2</td>
<td>0.16</td>
<td>0.05</td>
</tr>
<tr>
<td>CPP</td>
<td>25</td>
<td>2.2</td>
<td>0.11</td>
<td>0.05</td>
</tr>
<tr>
<td>PE</td>
<td>30</td>
<td>2.2</td>
<td>0.14</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Impact on Oxygen Barrier

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Thickness (µm)</th>
<th>O.D. (a.u.)</th>
<th>OTR Without Nexus-E (cm³/m² day)</th>
<th>OTR With Nexus-E (cm³/m² day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>12</td>
<td>2.2</td>
<td>0.53</td>
<td>0.56</td>
</tr>
<tr>
<td>BOPP</td>
<td>18</td>
<td>2.2</td>
<td>70.1</td>
<td>11.4</td>
</tr>
<tr>
<td>CPP</td>
<td>25</td>
<td>2.2</td>
<td>16.2</td>
<td>6.6</td>
</tr>
<tr>
<td>PE</td>
<td>30</td>
<td>2.2</td>
<td>46.2</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Surface energies > 56 mN/m enhancing layer nucleation

Improved lattice match and increased average chemical bond strength

Reduction on OTR correlates linearly with increase in bond strength

EXCELLENT OTR PERFORMANCE WITH > 3x IMPROVEMENT (POLYOLEFINS)
Improved Surface Energy Stability

No degradation in surface energy for ~ 4-5 weeks in challenging conditions

>> 2x improvement in shelf life after pre- & post treatment for BOPP, CPP etc.

Reduced oligomer migration & slip agent transfer following Nexus-E treatment

**EXCELLENT SURFACE ENERGY STABILITY**

- Nexus-E Power
- Nexus-E Flow

**Surface Energy (mN/m)**

- BOPP Nexus-E
- CPP Nexus-E

**Time After Deposition (Weeks)**

Without Nexus E
Summary

1. NEXUS-E POWER
   - Combinatorial pre-treatment system with charged species dose & energy control
   - Tunable modification of surface chemistry & near surface microstructure

2. NEXUS-E FLOW
   - Reactive oxygen pre- & post-treatments
   - AlOx like bond strength for metallized Al layers
   - Significant reduction of pinhole and improved barrier levels

User Benefits
- Compatibility and simplification of down-stream processes
- End-product quality improvement & cost reduction
- Barrier performance improvement up to factor 3

ADHESION ENHANCEMENT
Improved bond strength
>5.5 N/15 mm (PET)
>3.5 N/15 mm (BOPP)
>3.5 N/15 mm (CPP)