Atomic layer deposition for modification of surface properties

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One Stop for All ALD

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Outline

• Atomic layer deposition

• Surface modification with atomic layer deposition
  – Case I
    • TiN$_x$, Ti(Al)C$_x$ and Ti(Al)N$_x$C$_y$ on 304L SS
  – Case II
    • Al doped ZnO

• Conclusions
Atomic layer deposition

- Precision thin film deposition technique based on chemical vapor deposition
- First industrial application was electroluminescent displays
  - Manufactured in Finland since the 1980’s
  - Currently by Lumineq (Beneq)
ALD – Mechanism

Repeat ALD cycle $N$ times.
ALD – Advantages

- Conformality and large area uniformity
- Control over thickness and composition
- Low defect density
- Reproducability
- Low thermal budget


ALD – Available materials

V. Miikkulainen et al., J. Appl. Phys., 113 (2013) 021301
ALD – Applications

Electroluminescent displays

Integrated circuits

Permeation barriers

Protective coatings

Photovoltaics

Optical coatings

Batteries
Case I

- TiN$_x$, Ti(Al)C$_x$ and Ti(Al)N$_x$C$_y$ thin films
  - Substrate 304L stainless steel
  - ALD film growth
    - Precursors
      - TiN$_x$ from titanium tetrachloride (TiCl$_4$) and ammonia (NH$_3$)
      - Ti(Al)C$_x$ from titanium tetrachloride (TiCl$_4$) and trimethyl aluminium (TMA)
      - Ti(Al)N$_x$C$_y$ from TiCl$_4$, TMA and NH$_3$
    - Deposition temperature 430 °C
  - Coating thickness 100 nm
TiN$_x$, Ti(Al)C$_x$ and Ti(Al)N$_x$C$_y$ – Microscopy

- Uncoated 304L stainless steel
  - Rough surface morphology
TiN$_x$, Ti(Al)C$_x$ and Ti(Al)N$_x$C$_y$ – Microscopy
The O$_2$ plasma treatment was used to oxidise the film surface.

### Hydrophilicity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Post-treatment</th>
<th>Contact angle (DI H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated 304L</td>
<td>-</td>
<td>65°</td>
</tr>
<tr>
<td>TiN$_x$</td>
<td>-</td>
<td>0°</td>
</tr>
<tr>
<td>Ti(Al)C$_x$</td>
<td>-</td>
<td>45°</td>
</tr>
<tr>
<td>Ti(Al)N$_x$C$_y$</td>
<td>-</td>
<td>28°</td>
</tr>
<tr>
<td>TiN$_x$ O$_2$ plasma</td>
<td></td>
<td>0°</td>
</tr>
<tr>
<td>Ti(Al)C$_x$ O$_2$ plasma</td>
<td></td>
<td>0°</td>
</tr>
<tr>
<td>Ti(Al)N$_x$C$_y$ O$_2$ plasma</td>
<td></td>
<td>0°</td>
</tr>
</tbody>
</table>
TiN<sub>x</sub>, Ti(Al)C<sub>x</sub> and Ti(Al)N<sub>x</sub>C<sub>y</sub> – Corrosion

- 10% HCl @ 22 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Post-treatment</th>
<th>Corrosion rate / mm/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated 304L</td>
<td>-</td>
<td>0.63</td>
</tr>
<tr>
<td>TiN&lt;sub&gt;x&lt;/sub&gt;</td>
<td>-</td>
<td>0.48</td>
</tr>
<tr>
<td>Ti(Al)C&lt;sub&gt;x&lt;/sub&gt;</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>Ti(Al)N&lt;sub&gt;x&lt;/sub&gt;C&lt;sub&gt;y&lt;/sub&gt;</td>
<td>-</td>
<td>0.12</td>
</tr>
<tr>
<td>TiN&lt;sub&gt;x&lt;/sub&gt; O&lt;sub&gt;2&lt;/sub&gt; plasma</td>
<td></td>
<td>0.59</td>
</tr>
<tr>
<td>Ti(Al)C&lt;sub&gt;x&lt;/sub&gt; O&lt;sub&gt;2&lt;/sub&gt; plasma</td>
<td></td>
<td>0.30</td>
</tr>
<tr>
<td>Ti(Al)N&lt;sub&gt;x&lt;/sub&gt;C&lt;sub&gt;y&lt;/sub&gt; O&lt;sub&gt;2&lt;/sub&gt; plasma</td>
<td></td>
<td>0.10</td>
</tr>
</tbody>
</table>
TiN$_x$, Ti(Al)C$_x$ and Ti(Al)N$_x$C$_y$ – Corrosion

- TiN$_x$ – As deposited
- Ti(Al)C$_x$ – As deposited
- Ti(Al)N$_x$C$_y$ – As deposited
TiN$_x$, Ti(Al)C$_x$ and Ti(Al)N$_x$C$_y$ – Corrosion

TiN$_x$ – O$_2$ plasma

Ti(Al)C$_x$ – O$_2$ plasma

Ti(Al)N$_x$C$_y$ – O$_2$ plasma
Case II

- **Al doped ZnO**
  - Transparent n-type semiconductor
  - ALD film growth
    - \( \text{Al}_2\text{O}_3 \) deposited from trimethyl aluminium (TMA) and \( \text{H}_2\text{O} \)
    - ZnO deposited from diethyl zinc (DEZ) and \( \text{H}_2\text{O} \)
    - Deposition temperature 225 °C
  - Different concentrations of Al was doped into ZnO
    - Pure ZnO
    - AZO 49:1 (49 × ZnO + 1 × \( \text{Al}_2\text{O}_3 \))
    - AZO 24:1 (24 × ZnO + 1 × \( \text{Al}_2\text{O}_3 \))
    - AZO 12:1 (12 × ZnO + 1 × \( \text{Al}_2\text{O}_3 \))
    - Pure \( \text{Al}_2\text{O}_3 \)

Al:ZnO – Refractive index

- The composition can be digitally controlled

<table>
<thead>
<tr>
<th>Sample</th>
<th>n</th>
<th>Thickness of one supercycle (nm)</th>
<th>Total number of supercycles</th>
<th>Estimated total thickness (nm)</th>
<th>True total thickness (nm)</th>
<th>Estimated Al (at. %)</th>
<th>True at. % Al (via EDX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>100.0</td>
<td>103.0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Zn:Al=40:1</td>
<td>40</td>
<td>8.1</td>
<td>12</td>
<td>97.2</td>
<td>101.0</td>
<td>1.2</td>
<td>1.5</td>
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<td>Zn:Al=20:1</td>
<td>20</td>
<td>4.1</td>
<td>24</td>
<td>98.4</td>
<td>97.3</td>
<td>2.4</td>
<td>3.0</td>
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<tr>
<td>Zn:Al=13:1</td>
<td>13</td>
<td>2.7</td>
<td>37</td>
<td>99.9</td>
<td>95.0</td>
<td>3.7</td>
<td>7.3</td>
</tr>
<tr>
<td>Zn:Al=10:1</td>
<td>10</td>
<td>2.1</td>
<td>48</td>
<td>100.8</td>
<td>96.8</td>
<td>4.8</td>
<td>8.1</td>
</tr>
<tr>
<td>Zn:Al=8:1</td>
<td>8</td>
<td>1.7</td>
<td>59</td>
<td>100.3</td>
<td>96.8</td>
<td>5.9</td>
<td>10.9</td>
</tr>
<tr>
<td>Zn:Al=6:1</td>
<td>6</td>
<td>1.3</td>
<td>77</td>
<td>100.1</td>
<td>89.1</td>
<td>7.7</td>
<td>17.3</td>
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<tr>
<td>Zn:Al=5:1</td>
<td>5</td>
<td>1.1</td>
<td>91</td>
<td>100.1</td>
<td>86.3</td>
<td>9.1</td>
<td>24.6</td>
</tr>
</tbody>
</table>

TABLE I. List of samples used for obtaining data showing the ratio of Zn to Al cycles used to obtain various Al doping concentration. Here, n is the number of DEZ-DI water cycles inserted between consecutive TMA-DI water cycles. This constitutes a single supercycle. By repeating the supercycles, estimated total thickness is obtained. The true total thickness is based on measurement using spectroscopic ellipsometry. The estimated at. % Al is calculated by the method shown in text. The true at. % Al doping is obtained via EDX.

Al:ZnO – Transmission

- The films have over 80% transmission in the visible range.
- The unique properties of ALD can be utilized to model a thickness giving the optimized transmission.

![Graphs showing transmission of Al:ZnO films at different wavelengths.](image-url)
Al:ZnO – Electrical resistance

- Doping with Al greatly improves the conductivity of ZnO
  - Donor electrons
- An optimum is achieved at pulsing ratio 24:1
  - Too much Al resulted in insulating Al$_2$O$_3$ clusters
Conclusions

• Atomic layer deposition is a versatile tool for precision coating
• ALD TiN$_x$, Ti(Al)C$_x$ and Ti(Al)N$_x$C$_y$ coatings can be used to protect stainless steel
  – Ti(Al)N$_x$C$_y$ gives the best performance
• ALD enables control over Al doping into ZnO thin films
  – Lowest resistivity is achieved with 24:1 Zn:Al pulsing ratio
  – Transmission over 80 % over the visible range
Thank you

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