35 years of ALD

Tuomo Suntola, Picosun Oy
Conventional methods for compound film deposition

Heat treatment

Final crystallization

Nucleation

Vacuum evaporation

Sputtering

CVD
Buildup of thin film in source controlled deposition

Source control
Buildup of thin film in source controlled and in surface controlled deposition

Source control

Surface control
Atomic Layer Deposition
The ALD sequences for compound AB

Substrate surface
The ALD sequences for compound AB

Substrate surface

Introduction of precursor 1
supplying element A of compound AB
The ALD sequences for compound AB

Substrate surface

Introduction of precursor 1 supplying element A of compound AB

Completed monolayer of element A
The ALD sequences for compound AB

Substrate surface  Introduction of precursor 1 supplying element A of compound AB  Completed monolayer of element A  Introduction of precursor 2 supplying element B of compound AB
The ALD sequences for compound AB

Substrate surface  Introduction of precursor 1 supplying element A of compound AB  Completed monolayer of element A  Introduction of precursor 2 supplying element B of compound AB  Completed monolayer of element B

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The ALD sequences for compound AB

Substrate surface  Introduction of precursor 1 supplying element A of compound AB  Completed monolayer of element A
The ALD sequences for compound AB

Substrate surface

Introduction of precursor 1 supplying element A of compound AB

Completed monolayer of element A

-reduced monolayer density

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The ALD sequences for compound AB

Substrate surface

Introduction of precursor 1 supplying element A of compound AB

Completed monolayer of element A - reduced monolayer density

Introduction of precursor 2 supplying element B of compound AB
The ALD sequences for compound AB

Substrate surface

Introduction of precursor 1 supplying element A of compound AB

Completed monolayer of element A

Introduction of precursor 2 supplying element B of compound AB

Completed monolayer of element B

-reduced monolayer density
The ALD sequences for compound AB using exchange reactions
The ALD sequences for compound AB using exchange reactions

Substrate surface
AY

Introduction of precursor $BX_2$ for supplying element B of compound AB(X), removal of X as XY
The ALD sequences for compound AB using exchange reactions

Substrate surface AY

Introduction of precursor $BX_2$ for supplying element B of compound AB(X), removal of X as XY

Completed AB(X) surface

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The ALD sequences for compound AB using exchange reactions

- Substrate surface AY
- Introduction of precursor $BX_2$ for supplying element B of compound AB(X), removal of X as XY
- Completed AB(X) surface
- Introduction of precursor $AY_2$ supplying element A of compound AB(Y), removal of Y as XY
The ALD sequences for compound AB using exchange reactions

Substrate surface $AY$

Introduction of precursor $BX_2$ for supplying element B of compound AB(X), removal of X as $XY$

Completed AB(X) surface

Introduction of precursor $AY_2$ supplying element A of compound AB(Y), removal of Y as $XY$

Completed compound AB(Y) monolayer
Key tool for finding the ALE in 1974
Key tool for finding the ALE in 1974
Milestones in ALE-ALD development

Instrumentarium Lohja

Structure of thin film electroluminescent display

- Substrate glass
- Passivation layer (ion barrier)
- Dielectric layers
- Light emitting layer, ZnS(Mn)
- Electrodes

- Passivation layer
- Black back layer

EL-character module
Milestones in ALE-ALD development

Ulf Stom and Tuomo Suntola look at a prototype of the new EL-display in 1984
Milestones in ALE-ALD development

- 1974: Demonstration of ALE for ZnS (Instrumentarium)
- 1980: Travelling wave reactor for ZnS and oxides (Lohja)
- 1990: Introduction of ALE-EL device performance
- 2000: Production line for flat-panel matrix displays P-250 >> P-400 reactors
- 2010: Commercial production of ALE-EL panels by Lohja > Planar International

Companies:
- Instrumentarium
- Elcoteq
- Lohja
- Planar International
## Research activities in ALE-ALD

<table>
<thead>
<tr>
<th>Year</th>
<th>Search for perfection in thin films for EL, ZnS &amp; dielectrics</th>
<th>ALE &amp; precursor chemistry</th>
<th>Search for perfection in III-V single crystals and super-grid structures</th>
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<tbody>
<tr>
<td>1974</td>
<td>Instrumentarium, Lohja</td>
<td>ALE and precursor chemistry, Helsinki University of Technology</td>
<td>University &amp; corporate groups in Japan</td>
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<td>1980</td>
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<td>Helsinki University of Technology</td>
<td>University groups in the US</td>
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<td>1990</td>
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<tr>
<td>2000</td>
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Milestones in ALE-ALD development

- 1974: Demonstration of ALE for ZnS (Instrumentarium)
- 1980: Travelling wave reactor (Lohja)
- 1990: Exchange reactions for ZnS and oxides
- 1990: Introduction of ALE-EL device performance
- 2000: Introduction of first ALE-EL product
- 2000: Introduction of ALE for catalytic surfaces
- 2010: Commercial production of ALE-EL panels by Lohja > Planar
- 2010: Demonstration of ALE-CdTe solar cell performance
- 2010: F-120 reactors (Microchemistry)
## Research goals in ALE-ALD

<table>
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<td>Heterogeneous catalysts, advanced surface chemistry</td>
<td>Microchemistry, Helsinki University of Technology</td>
<td>Colorado State University</td>
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<tr>
<td>Diffusion barriers and passivation layers enabling conformality in semiconductor devices</td>
<td>Microchemistry, Helsinki University</td>
<td>Semiconductor equipment manufacturers</td>
<td>University groups</td>
</tr>
<tr>
<td>Ultra-thin and high-k dielectrics for semiconductor devices</td>
<td></td>
<td>Semiconductor manufacturers</td>
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## Research goals in ALE-ALD

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<td></td>
<td></td>
<td>Semiconductor equipment manufacturers</td>
</tr>
<tr>
<td>Molecular lay-up of oxide surfaces</td>
<td>Prof. Aleskovski, St. Petersburg</td>
<td></td>
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</tbody>
</table>

Milestones in ALE-ALD development in Finland

1974: demonstration of ALE for ZnS (Instrumentarium)
1980: travelling wave reactor (Lohja)
1990: exchange reactions for ZnS and oxides
2000: introduction of ALE-EL device performance
2010: introduction of first ALE-EL product

- production line for flat-panel matrix displays P-250 >> P-400 reactors
- Commercial production of ALE-EL panels by Lohja > Planar

- F-120 reactors (Microchemistry)
- demonstration of ALE-CdTe solar cell performance
- introduction of ALE for catalytic surfaces
- F-450, F-850 reactors for large surfaces
- F-200 reactors for wafers
- Wafer cluster tool reactors (ASM)
- F-120 reactors (Nanofin)

- Sunale reactors (Picosun)
- TFS 500 reactor (Beneq)

Tuomo Suntola, Picosun Oy
Tool for the demonstration of ALE in 1974
ALE growth of ZnS in Aug/Sept 1974

Hexagonal ZnS: monolayer 3.13 Å
n=2.36

1/3 x monolayer

0.6
0.4
0.2
0
0 10 20 30 minutes

320 °C
10⁻⁴ torr
3x10⁻³ torr
100 °C
2 c/s

4x10⁻⁵ torr
2x10⁻² torr
360 °C
Milestones in ALE-ALD development
ALD for advanced semiconductor and nanotechnology manufacturing

F-850 reactor, Microchemistry in 1998
Pulsar, ASM
SUNALE™ ALD Reactors, Picosun Oy
ALD for advanced semiconductor and nanotechnology manufacturing
Conformal growth mode

Superlattice by NEC, Japan
Conformal growth mode
Research goals in ALE-ALD

Diffusion barriers and passivation layers enabling conformality in semiconductor devices

Ultra-thin and high-k dielectrics for semiconductor devices
Coating of microslices

110°C, aspect ratio >25
standard pulsing sequence
conformality >96%

Samples by Riikka Puurunen, VTT Finland
Conformality at low processing temperature

110°C, aspect ratio >25
standard pulsing sequence
conformality >96%

Samples by Riikka Puurunen, VTT Finland
Conformality at low processing temperature

110°C, aspect ratio >25
standard pulsing sequence
conformality >96%

Samples by Riikka Puurunen, VTT Finland

Tuomo Suntola, Picosun Oy
Extreme of conformality: heterogeneous catalysts
Extreme of conformality: heterogeneous catalysts

<table>
<thead>
<tr>
<th>precursor</th>
<th>surface species / support</th>
<th>density of atoms [ /nm² ]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at top</td>
<td>at bottom</td>
</tr>
<tr>
<td>ZrCl₄ / SiO₂</td>
<td>1.44 ± 0.04</td>
<td>1.44 ± 0.04</td>
</tr>
<tr>
<td>WOCl₄ / Al₂O₃</td>
<td>1.81 ± 0.06</td>
<td>1.81 ± 0.05</td>
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<tr>
<td>Ni(acac)₂ / Al₂O₃</td>
<td>2.52 ± 0.25</td>
<td>2.25 ± 0.11</td>
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<tr>
<td>Cr(acac)₃ / SiO₂</td>
<td>0.32 ± 0.01</td>
<td>0.30 ± 0.00</td>
</tr>
<tr>
<td>Mg(thd)₂ / SiO₂</td>
<td>0.98 ± 0.08</td>
<td>0.82 ± 0.08</td>
</tr>
</tbody>
</table>

Tuomo Suntola, Picosun Oy
High-k + Metal Gate Transistors

High-k + metal gate transistors provide significant performance increase and leakage reduction, ensuring continuation of Moore’s Law
High-k + Metal Gate Transistors

- Integrated 45 nm CMOS process
- High performance
- Low leakage
- Meets reliability requirements
- Manufacturable in high volume

“The implementation of high-k and metal gate materials marks the biggest change in transistor technology since the introduction of polysilicon gate MOS transistors in the late 1960s”

Gordon Moore

Jan. 2007
Wafer Size Conversion history

100 mm
1970

Re-edited from: ALD: In-situ chemistry at molecular level
Wafer Size Conversion history

<table>
<thead>
<tr>
<th>100 mm</th>
<th>150 mm</th>
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<tbody>
<tr>
<td>1970</td>
<td>1980</td>
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</tbody>
</table>

Re-edited from: ALD: In-situ chemistry at molecular level
Wafer Size Conversion history

100 mm 150 mm 200 mm

Re-edited from: ALD: In-situ chemistry at molecular level
Wafer Size Conversion history

100 mm  150 mm  200 mm  300 mm

Re-edited from: ALD: In-situ chemistry at molecular level
Wafer Size Conversion history

Re-edited from: ALD: In-situ chemistry at molecular level
## Wafer Size Conversion history

<table>
<thead>
<tr>
<th>Size</th>
<th>Year</th>
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<tbody>
<tr>
<td>100 mm</td>
<td>1970</td>
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<tr>
<td>150 mm</td>
<td>1980</td>
</tr>
<tr>
<td>200 mm</td>
<td>1990</td>
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<tr>
<td>300 mm</td>
<td>2000</td>
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<tr>
<td>450 mm</td>
<td>2010</td>
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<tr>
<td>675 mm</td>
<td>2020</td>
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</tbody>
</table>

Re-edited from: ALD: In-situ chemistry at molecular level

Tuomo Suntola, Picosun Oy
The MOS elements – 1970’s

![Periodic Table of the Elements](image)

Source: P. Gargini, International Technology Roadmap for Semiconductors
The MOS elements – 1980’s

Source: P. Gargini, International Technology Roadmap for Semiconductors
The MOS elements – nanotechnology

Source: P. Gargini, International Technology Roadmap for Semiconductors
Number of active elements on an IC chip

Moore’s law for the complexity of IC’s

From 1960 to 1970, ‘complexity’ is the number of components as initially described by Moore. After 1970, it was often cited as the number of bits in a DRAM or the number of transistors in a microprocessor.

Source: Semiconductor International
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Moore’s law for the complexity of IC’s

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Source: Semiconductor International
Gate Dielectric Scaling (High-K)

Thinner equivalent gate oxide increases transistor performance

Source: P.Gargini, International Technology Roadmap for Semiconductors
1st International Symposium on Atomic Layer Epitaxy, 1990

From left:
Prof. Konagai, Dr. Nykänen†, Dr. Suntola, Prof. Niinistö, Prof. Nishizawa, Prof. & Mrs. Bedair
First Symposium on Atomic Layer Epitaxy

VTT 1984