Spatial Atomic Layer Deposition (ALD): a novel disruptive technology
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TNO is...

• The Dutch research organization for applied scientific research

• Established by law in 1932

• Independent of public and private interests

• Contract R&D institute for industry and government

• Annual turnover > 500 M€

• Employees > 4,000
About TNO in The Netherlands

Sites in Eindhoven

University campus

Holst Centre at High-Tech Campus (TNO and imec)
Principles: ALD of Al$_2$O$_3$ from Al(CH$_3$)$_3$ and H$_2$O

Atomic Layer Deposition

- sequential pulsing of precursors
- purge/ vacuum between all pulses
- self-limiting (ligand exchange)
- step conformal, e.g. in trenches
What makes ALD a powerful technique

- Very high film quality
- No particles, no pinholes
- Thickness control on an atomic scale
- Superior conformality
  - Ability to follow complex and 3D geometries
- Wide range of materials
  - Oxides, nitrides, sulfides, …
  - Metals
  - Hybrid organic – inorganic materials
  - Even polymers

- But... s-l-o-w......
ALD offers many novel opportunities....

- Yet, today, ALD is used almost exclusively in microelectronics mass manufacture

- A large potential of ALD for cost-effective, large area & flexible applications calls for ALD in a different, cost-efficient way...
Using ALD in a different, cost-efficient way...

- Faster
- Not limited by substrate size, material and flexibility
- Continuous, in-line
- Lower costs (e.g. precursor consumption)
- Atmospheric conditions

► Commercial use started only around 2008: Spatial (atmospheric) ALD
Spatial Atomic Layer Deposition

Gas bearing: a gas lubricated bearing
- Non-contact, no stick-slip, mechanically robust

Dual function in Spatial ALD:
- Bearing between injector and substrate
- Separation of reactive gases
Spatial ALD at TNO: rotary R&D reactor

- **Spatial separation** of half-reactions, instead of time-separated
- No parasitic deposition, high precursor yield, atmospheric pressure
- Deposition rate: > 1 nm/s! ~**100x faster**!
- Materials deposited so far by TNO: Al$_2$O$_3$, TiO$_2$, HfO$_2$, ZnO, ZnO:Al, ZnO:In, InZnO, InGaZnO, ZnSnO$_x$ silver, Alucone (MLD)
### Mind: ‘fast’ is relative ...

<table>
<thead>
<tr>
<th>Spatial ALD</th>
<th>Hair</th>
<th>1.25 cm/month</th>
<th>5 nm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nails</td>
<td>0.1 mm/day</td>
<td>1 nm/s</td>
<td></td>
</tr>
<tr>
<td>Mount Everest</td>
<td>1 cm/year</td>
<td>0.3 nm/s</td>
<td></td>
</tr>
<tr>
<td>ALD</td>
<td>Lichen</td>
<td>1 mm/year</td>
<td>0.03 nm/s</td>
</tr>
<tr>
<td>Stalactites</td>
<td>0.13 mm/year</td>
<td>0.004 nm/s</td>
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</table>
Proven concept, commercially available

- **In-line** spatial ALD reactors for c-Si solar cell manufacturing

**PRESS RELEASE** **Leuven, Belgium, September 24, 2012**

*Imec, RENA and SoLayTec present innovative ALD passivation for high-efficiency i-PERC Silicon Solar Cells* (165μm), large area (156x156mm2) i-PERC-type Silicon solar cells with ALD (atomic layer deposition) passivation achieving a cell efficiency of 19.6% without selective emitter using an industrial screen printing process flow.
Opportunities for Spatial ALD

- Encapsulation & barriers (e.g. for OLEDs/OPV)
- Packaging
- Transparent conductors (e.g. for solar cells)
- Dielectric- and passivation layers and amorphous oxide semiconductors (e.g. for TFTs)
- Light management (e.g. for solar cells and OLEDs)
- Hybrid or organic films by Molecular Layer Deposition Interface engineering (e.g. CIGS)
- Paper- or textile-based electronics
- Optical coatings
- Photovoltaics, OLEDs, displays, glazing, energy storage, sensors, catalysis,...
Challenges to be addressed

- How fast and how large can we go?
- Uniformity
- Cost-efficiency
- How to get good performance at low deposition temperatures
- How to extend the process-toolbox
  - Plasma, ozone, UV, lasers, characterization, ...
- How to do patterned deposition, and how small can we go?
- Can we do Spatial MLD?
- Can we use other precursors (cheaper, safer, effect of purity, ....)?
- How to do spatial ALD on polymer substrate?
- ......

Spatial ALD on flexible substrates

Spatial ALD mainly used on rigid substrates
► Does it work for flexible substrates?

Challenges:
• Foil deformation and strain
• Contamination
• Thick films
• Large substrates
• Temperature limitations
Roll-to-roll spatial ALD concepts

Ultratech-Cambridge Nanotech (USA)

Lotus Applied Technology (USA)

Beneq Oy (Finland)
Roll-to-roll spatial ALD: TNO’s approach

- Center piece: foil surrounding a drum with several reaction zones and gas-bearings
- Foil moves clockwise (slowly)
- Spatial ALD injector rotates counterclockwise (fast)
- Combination ► high deposition rate
- Flows interrupted at bottom passage
- No mechanical contact on deposition side
- Flexibility in foil and layer thickness
- Compact
Reactor layout

www.youtube.com/watch?v=PS65f635L8w
Spatial ALD injector drum

- side wall with holes for gas inlets/outlets
Disks for contactless gas/precursor supply

- Gases are supplied via circular grooves
- Gas bearings as contactless seals
- Supply is interrupted at the bottom part of the disk
R2R Spatial ALD reactor TNO (in real life)

http://www.youtube.com/watch?v=NJUINHnys0g
First test results

- It works....

- Homogeneous Al₂O₃ deposition: thickness of ~25 nm at 1 m/min web speed and 60 rpm drum rotation

- 2Q2013: cleanroom environment installed

- Film property measurements are pending (e.g. WVTR)

40 nm alumina on PEN
WVTR = 1.5x10⁻⁵ g/m²/day

12 days 20 °C/50 % RH
Results: Al-foil

- Tool can also be used for metal foil
- Kitchen-grade Al-foil (~15 μm) (source: local supermarket)
- 1000 ALD cycles; ~ 100 nm Al₂O₃
Results: Al-foil

- Protective properties of ALD film studied by Cu electroplating

Uncovered back side (no $\text{Al}_2\text{O}_3$): Cu plated on the Al

ALD $\text{Al}_2\text{O}_3$ covered front side: no Cu plating ►confirmed by XRF
Examples of applications
Trench filling with spatial ALD of Al$_2$O$_3$ (200 °C, 1 atm.)

600 cycles (70 nm)
~0.12 nm/cycle
2 Hz rotary reactor
$\rho_{TMA}$~ 3 mbar
$\rho_{H2O}$~ 123 mbar
Step coverage ~ 80%

Time scale $\tau =$13.5 ms

Courtesy:

600 cycles (70 nm)
~0.12 nm/cycle
2 Hz rotary reactor
$\rho_{TMA}$~ 3 mbar
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Step coverage ~ 80%

Time scale $\tau =$13.5 ms

Courtesy:
Thin film encapsulation

Water vapor infiltration: major reliability issue in large area electronics
- (e.g. ZnO in CIGS, cathode in OLEDs, organic semiconductors)

Encapsulant required to provide barrier against water diffusion

Benchmarks:
- Water Vapor Transmission Rate (WVTR, g/m²/day)
- Oxygen Transmission rate (OTR, cm³/m²/day/atm)
- Pinhole density
Encapsulation

- **ALD Al₂O₃ thin films with excellent barrier properties**
  - Low intrinsic WVTR ($\sim 10^{-6} - 10^{-5}$ g/m²/day)
  - Low intrinsic pinhole density (if done properly)

- **ALD Al₂O₃ as a moisture/oxygen diffusion barrier**
  - On/in paper for packaging for food and medical
  - As single film on e.g. CIGS solar cells
  - Combined with stacks for e.g. lighting and displays

- **Challenges**
  - Upscaling! Cost-efficient large-area deposition, R2R or S2S
  - Low-temperature processing
  - Optimize performance (WVTR and pinholes)

![Graph showing resistance over time for different samples of Al₂O₃](image)
Spatial ALD for Thin-Film Transistors: gate dielectric

- **ALD grown gate dielectrics (e.g. Al₂O₃, HfO₂, ...)**
  - Low leakage currents, good stability

- **Firsts tests using Spatial ALD Al₂O₃ are promising**
  - Low-temperature process (100 °C), not optimized
  - Acceptable leakage current, no breakdown at 4 MV/cm
  - Results similar to conventional ALD films
Spatial ALD of TFT channels: InGaZnO and ZnSnO

Method developed for making multi-component oxides by pre-mixing
- No delta-doping/nanolaminates: uniform composition
- Accurate control of composition and thickness

Example: amorphous InGaZnO and ZnSnO
- Amorphous semiconductor, used as channel in TFT
- First TFTs made with S-ALD InGaZnO!
  Promising results, but further optimization required
Integration of atmospheric pressure plasma source

- ‘Blanket’ plasma: room temperature ALD, metals (e.g. silver)

- DBD μ-plasma source for maskless patterning

40 nm Ag on glass with 1 source

~100 nm Al₂O₃ tracks on Si with 5 sources

New Shared Research Program on Spatial ALD in the Holst Centre program matrix

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<th>Technology Programs: development of key technologies</th>
<th>Technology Integration Programs: windows on application areas, guiding choices in the TPs</th>
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<td>Ultra-Low Power DSP</td>
<td>Printed Organic Lighting and Signage</td>
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<td>Ultra-Low Power Wireless Systems</td>
<td>Body Area Networks</td>
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<tr>
<td>Micropower Systems</td>
<td>Flexible OLED Displays</td>
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<td>Integration Techn. for Flex. Systems</td>
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<td>Printed Conductive Structures</td>
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<td>Organic and Oxide Transistors</td>
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<td>Patterning for Flexible Systems</td>
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Spatial ALD

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Acknowledgments

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Raymond Knaapen (*R2R*)
Frank Grob (*R2R*)
Mattij van den Boer (*R2R*)
Fieke van den Bruele (*MLD*)
Mireille Smets (*MLD*)
Fred Roozeboom (*ALD, RIE*)

**TNO (*R2R*)**
Ruud Olieslagers
Dennis van de Berg
Adriaan Lankhorst
Joop van Deelen

**Holst Centre (*TFTs*)**
Brian Cobb
Ashutosh Tripathi

**Students**
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Akhilc Sharma (*InGaZnO*)
Bart de Raadt (*ZnSnO*$_x$)
Joep van Lieshout (*R2R*)
Sara Motahari

THANK YOU!
Temporal plasma-ALD of SiO$_2$ and Al$_2$O$_3$

Saturation curves for SiO$_2$ and Al$_2$O$_3$

ALD cycle:

- Dose time (ms)
- Purge time (s)
- Plasma time (s)
- Plasma purge (s)

200 ºC

Temporal plasma-ALD of SiO$_2$ and Al$_2$O$_3$

Saturation curves for SiO$_2$ and Al$_2$O$_3$

Conformality in 30:1 trench

**SiO\textsubscript{2}** 200 °C
90 ms precursor dose
5 s purge
4.5 s plasma O\textsubscript{2}
6 s purge
95-100 % conformal

**Al\textsubscript{2}O\textsubscript{3}** 200 °C
30 ms
5 s
4.5 s
1.5 s
50 % conformal

SiO\textsubscript{2} at 50 °C also possible with PE-ALD

Temporal plasma-ALD of SiO$_2$ and Al$_2$O$_3$ / Conformality at 100 °C

Plasma exposure times: 0.5 s (■) and 2s

SiO$_2$ at 50 °C also possible with PE-ALD

→ Suggests a higher recombination rate of O* radicals on Al$_2$O$_3$ than on SiO$_2$ surfaces…
Conformality SiO$_2$ vs. Al$_2$O$_3$

Role of O-radicals

Low recombination loss probabilities $r$ for O-radicals on oxides:

<table>
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<tr>
<th>Oxide</th>
<th>Low Recombination Loss Probability ($r$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>$2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>$2.1 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

- **Recombination** (of O-radicals) appears to play no significant role in conformality of SiO$_2$, even at 100 °C for AR = 30
- Also holds for PEALD from 3DMAS/O$_2$ in AR = 60

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*** Niinistö, Leskelä, *et al.* ALD 2011, p.66