FINNISH CENTRE OF EXCELLENCE
IN
ATOMIC LAYER DEPOSITION

2012–2017

# Atomic Layer Deposition – Finnish innovation for making advanced materials

## Research at University of Helsinki


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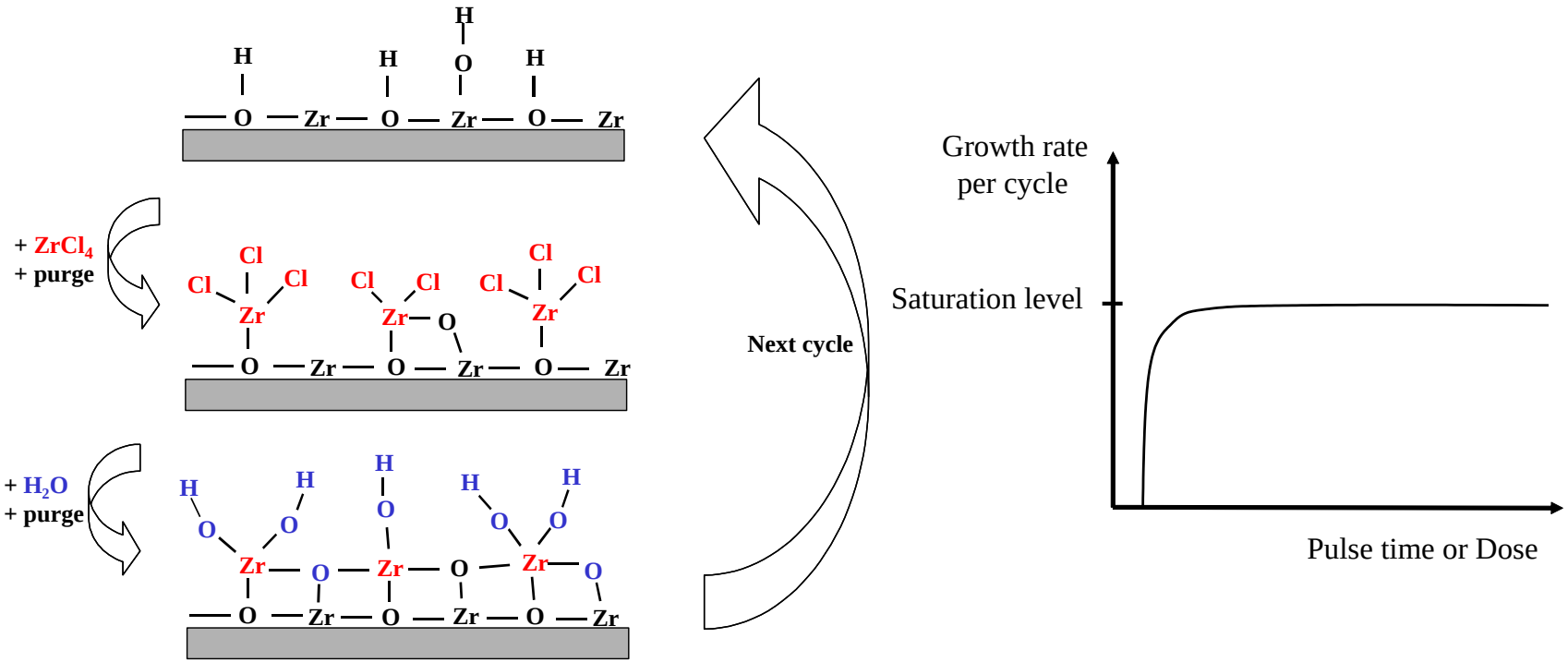
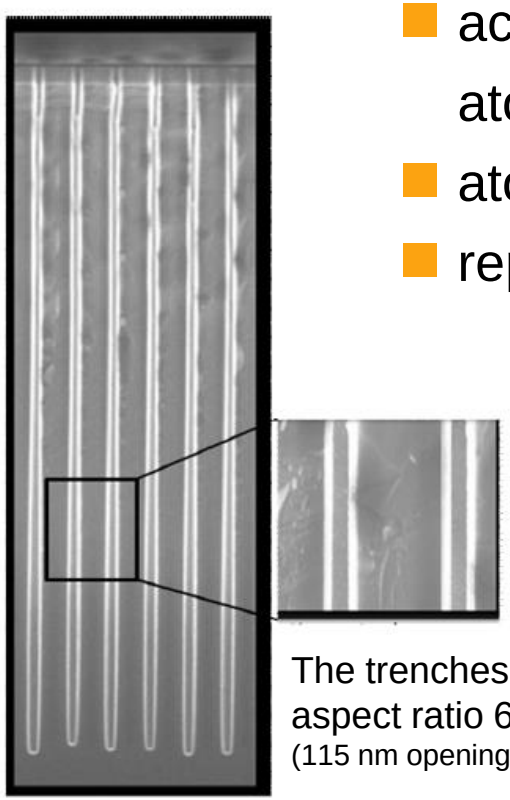
# Atomic Layer Deposition

- a unique method to grow **superior thin films**
- **alternately** supplied gaseous precursors undergo **saturative** surface reactions → **self-limiting thin film growth** (no gas phase reactions, no decomposition)



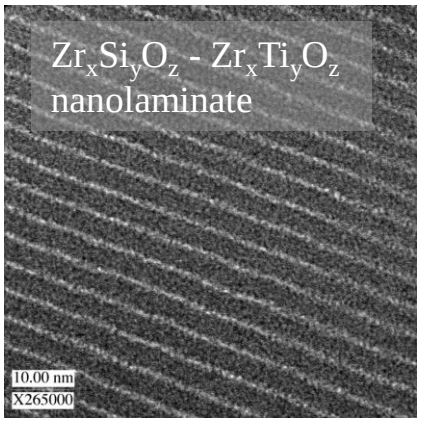
# Advantages of ALD – consequences of the self-limiting growth

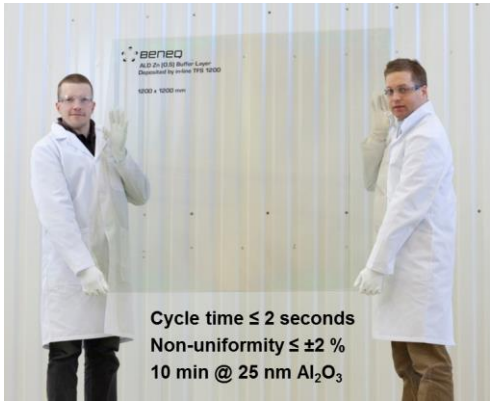
- excellent conformality
- large area uniformity: large substrates, large batches
- accurate and easy film thickness control down to an atomic level
- atomic level control of film composition
- reproducibility

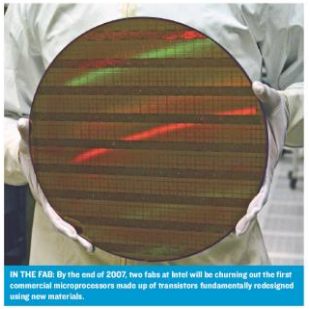



The trenches have an aspect ratio 60:1
(115 nm opening, 6.75 µm depth).

Kariniemi et al. J. Vac. Sci. Technol. A 30 (2012) 01A115



30 Å with 1 Å ($10^{-10}$ m) accuracy and uniformity over 300 mm silicon wafer: 1 : 3 000 000 000

# Finnish roots of ALD

- introduced with a name of Atomic Layer Epitaxy in 1974 by Dr. Tuomo Suntola and coworkers for preparation of electroluminescent (EL) displays

**United States Patent** [19]
**Suntola et al.**

[11] **4,058,430**
[45] **Nov. 15, 1977**

[54] **METHOD FOR PRODUCING COMPOUND THIN FILMS**

[76] Inventors: **Tuomo Suntola**, Riihikallio, 02610 Espoo 61, Finland; **Jorma Antson**, Urheilutie 22, 01350, Vantaa 35, Finland

[21] Appl. No.: **635,233**

[22] Filed: **Nov. 25, 1975**

[30] **Foreign Application Priority Data**
Nov. 29, 1974 Finland ..... 743473

[51] **Int. Cl.**[2] ..... **B05D 5/00**; B05D 5/12
[52] **U.S. Cl.** ..... **156/611**; 118/49; 156/612; 427/87; 427/248 B; 427/248 E; 427/248 J; 427/255
[58] **Field of Search** ..... 427/250, 399, 87, 248 B, 427/248 E, 248 J, 255; 156/600, 612, 611; 118/49

[56] **References Cited**
U.S. PATENT DOCUMENTS

| | | | |
|---|---|---|---|
| 3,489,621 | 1/1970 | Sirtl | 427/250 X |
| 3,493,430 | 2/1970 | Manasevit | 427/250 X |
| 3,556,837 | 1/1971 | Hammond | 427/250 |
| 3,576,670 | 4/1971 | Hammond | 427/250 X |
| 3,839,084 | 10/1974 | Cho et al. | 156/611 |
| 3,862,859 | 1/1975 | Ettenberg et al. | 156/600 X |
| 4,000,716 | 1/1977 | Kurata et al. | 427/87 X |

OTHER PUBLICATIONS

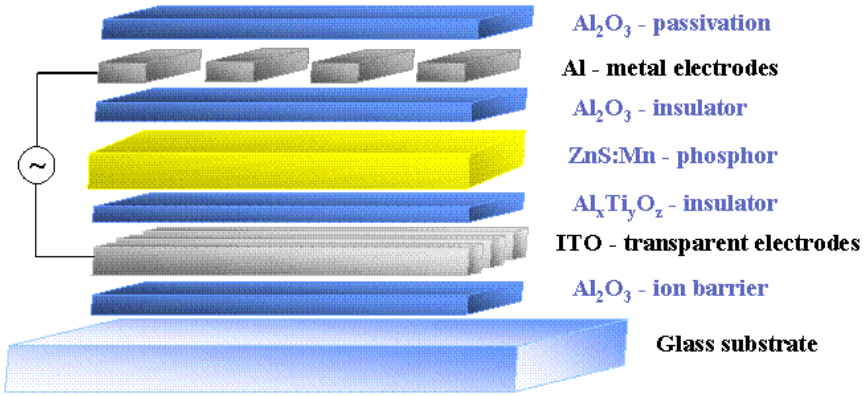
Curzon et al., J. Phys. D. Appl. Phys. vol. 5, No. 5 (1972), pp. 1046–1048.

*Primary Examiner*—Harry J. Gwinnell
*Attorney, Agent, or Firm*—Steinberg & Blake

[57] **ABSTRACT**

A method is provided for growing highly oriented compound thin films on a substrate by subjecting the substrate to the vapor of a first single element which can react with the surface at a temperature sufficiently high for the reaction to occur which forms a single atomic layer of the first single element on the surface and then subjecting the thus formed surface with a first single element atomic layer thereon to the vapor of a second single element which can react with the first single element at a temperature sufficiently high for the reaction to occur so that a single atomic layer of the second single element is formed on the surface bound to the first single element. This procedure can then be repeated alternately subjecting the surface to the vapors of the first single element then to the second single element, etc. until the compound film reaches a desired thickness. There is further provided an apparatus for carrying out this method comprising a vacuum chamber with evacuating means, a support for supporting a substrate, sources for at least two vapors of two different single elements and operating means for providing on the substrate first a single atomic layer of one of the elements, and then a single atomic layer of the other of the elements.

**8 Claims, 7 Drawing Figures**



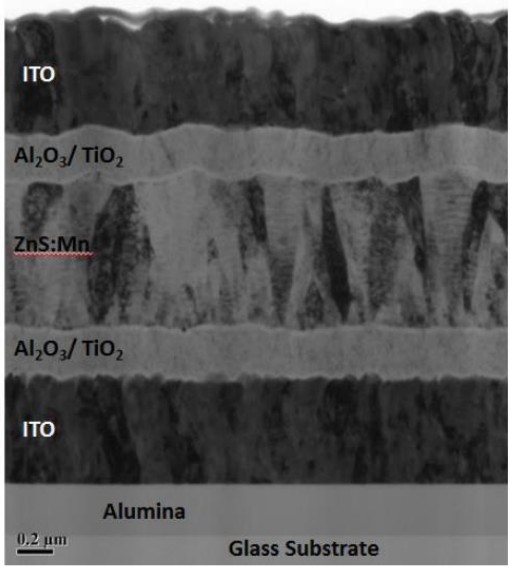
# Finnish roots of ALD

Proof of concept for ALD:

Beneq factory in Espoo, Finland

EL display production 24/7 since 1985; > 3 million displays produced

Transparent display with both electrodes made from ITO.



# ALD tool companies in Finland

- tools and solutions for all possible application areas
- coating services (Beneq)
- all in active collaboration with University of Helsinki

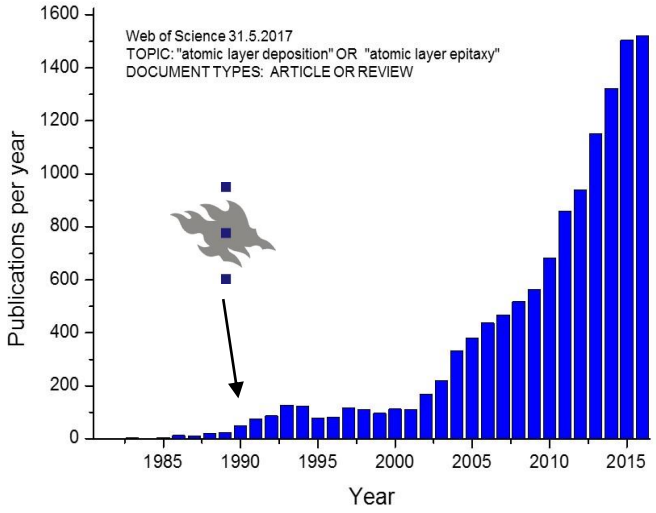
ASM

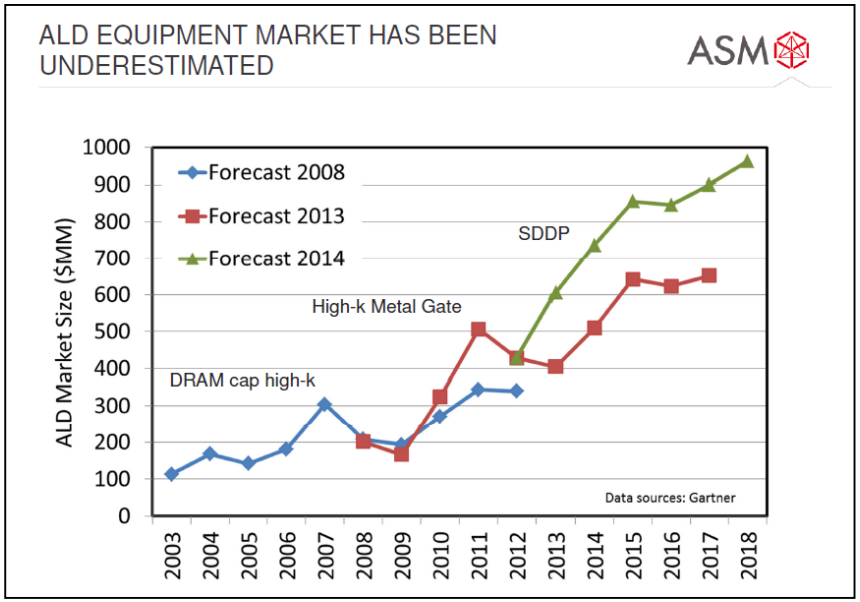
beneq

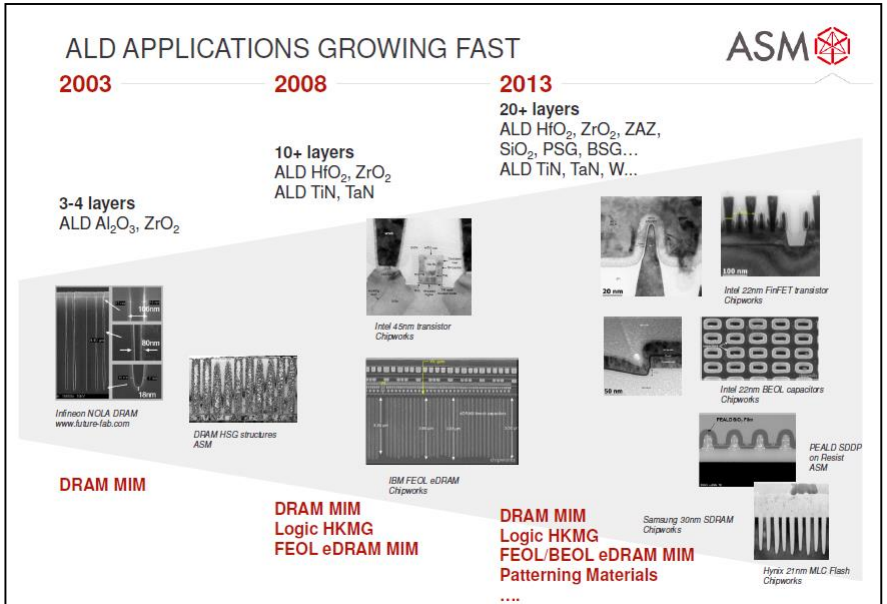
Picosun

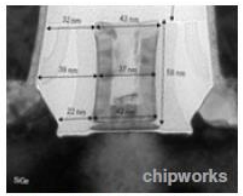
Since 2018 owned by Qingdao Sifang
SRI Intellectual Technology Co. Ltd.

# ALD getting global through semiconductor industry

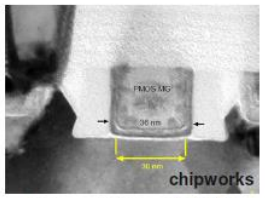


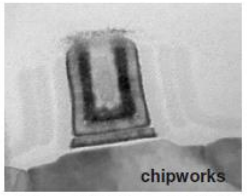



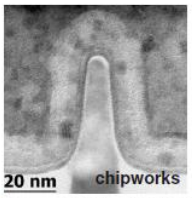

45nm HK first RPMG
Planar FET




32 nm HK last RPMG
Planar FET




28nm HK first RPMG
Planar FET

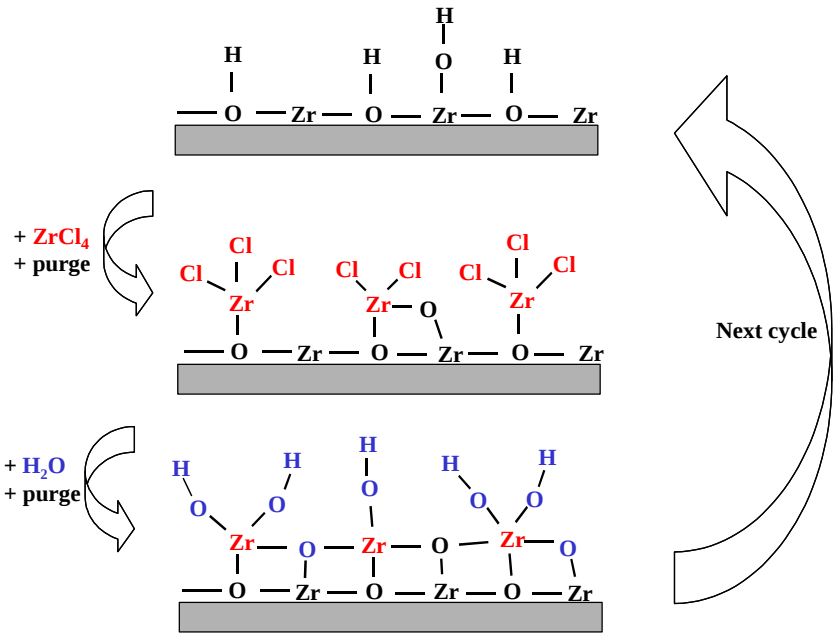



22nm HK last RPMG
FinFET

Ivo Raaijmakers, ASM International, ALD conference 2014, Kyoto

# Success of ALD is built on chemistry

To deposit any material of an interest, proper precursors must be found.




## Requirements to ALD precursors

**must**

- sufficient volatility
- aggressive and complete reactions
- thermal stability (no self-decomposition)
- no etching of the film or substrate material
- no dissolution into the film substrate
- sufficient purity

often contradictory

---

**nice to have**

- gases or highly volatile liquids
- high growth rate per cycle (small molecule, high reactivity)
- unreactive volatile byproducts
- inexpensive
- easy to synthesize and handle
- nontoxic and environmentally friendly

High-k oxide precursor market:
$258M in 2015
~$400M in 2020

(TECHECT 2016 Critical Materials Report)

# Helsinki ALD – thin films and nanostructured materials

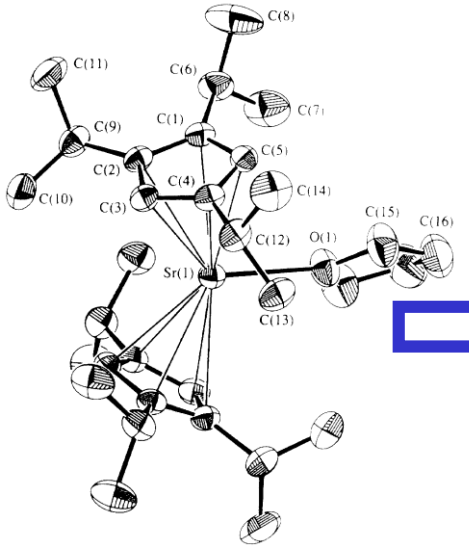
- professor Mikko Ritala
  professor emeritus Markku Leskelä
- in total about 25 people
- started in 1990

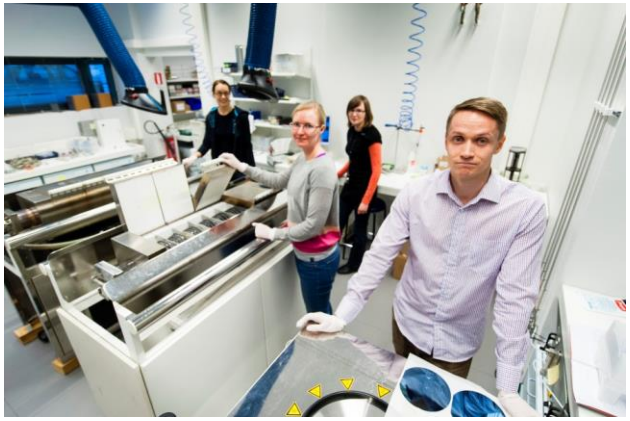
- nearly 500 papers and several key patents
  - both leaders are ISI highly cited in materials science
- worldwide collaboration network, also with industry
- focus is in the *chemistry of ALD*, precursors and processes, but the research covers also integration of ALD processes to various applications

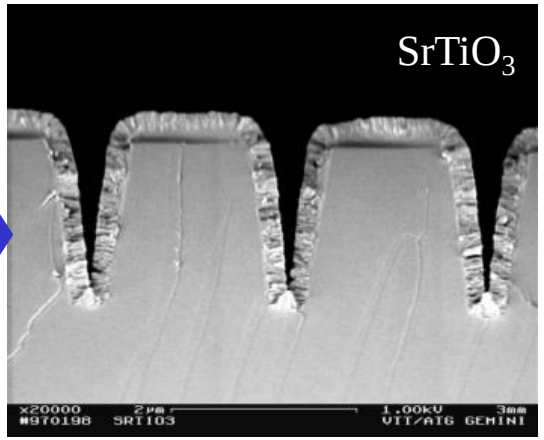
# ALD research at University of Helsinki

Starting from **precursor chemistry**, new well characterized **ALD processes and materials** are developed and taken into the first stages of applied research, in a **wide range of application areas**.

$$Sr(C_5iPr_3H_2)_2 + H_2O + Ti(OiPr)_4 + H_2O \rightarrow SrTiO_3$$






$Sr(C_5{}^{i}Pr_3H_2)_2(THF)$

Vehkamäki et al., Electrochem. Solid State Lett. 2 (1999) 504.

# ALD research at University of Helsinki

Main facilities

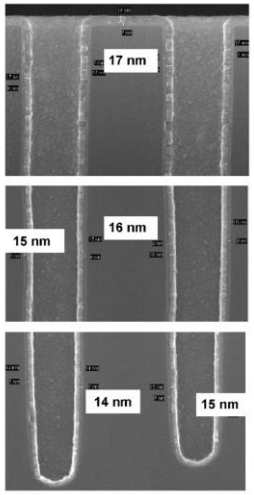
- eight F120 ALD reactors (ASM Micrcohemistry)
  - one with a quadrupole mass spectrometer and quartz crystal microbalance for in situ mechanism studies
- two R150 ALD reactors (Picosun), one with UV-lamp
- TFS 200 (PE)ALD reactor (Beneq)

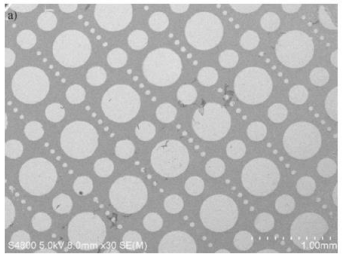
F120 by Microchemistry

SUNALE™ R150 by Picosun

TFS 200 by Beneq

# Current and recent ALD research topics



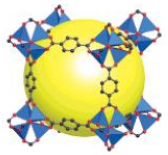
E. Färm et al. J. Electrochem. Soc. 2010, 157, K10

- new precursors
- reaction mechanism studies by QMS and QCM

- $Ge_2Sb_2Te_5$ and related phase change materials
- thermoelectric materials
- metals and nitride barriers for metallizations, electrodes and in general
- high-k oxides and precursors for DRAM, FERAM and MOSFETs
- 2D metal chalcogenides
- low-k insulators

- selective area ALD
- radical enhanced ALD
- photo ALD
- nanostructures by templating and ALD

- hydroxyapatite films for medical aplications
- corrosion protection coatings
- fuel cell and solar cell materials
- materials for thin film Li ion batteries
- fluorides for optics
- inorganic-organic hybrid materials
- x-ray optics



# ALD materials made at University of Helsinki

| | |
|---|---|
| Oxides | |
| Dielectric | $Al_2O_3$, $TiO_2$, $ZrO_2$, $HfO_2$, $Ta_2O_5$, $Nb_2O_5$, $V_2O_5$, CuO, $CoO_x$, $RE_2O_3$, $SiO_2$, $SrTiO_3$, $BaTiO_3$, $SrTa_2O_6$, $SrBi_2Ta_2O_9$, $Bi_4Ti_3O_{12}$, $BiFeO_3$ |
| Transparent conductors | $In_2O_3$, $In_2O_3$:Sn, $In_2O_3$:Zr, $SnO_2$, ZnO, ZnO:Al |
| Metallic oxides | $Rh_2O_3$, $IrO_2$, PdO, $PtO_x$ |
| Nitrides | |
| Semiconductors/Dielectric | AlN, $Ta_3N_5$ |
| Metallic | TiN, Ti-Al-N, TaN, Ta-Si-N, NbN, MoN, $ReN_x$ |
| Metals | Ru, Pt, Ir, Pd, Rh, Os, Cu, Ag, Sb, Au, Re |
| Intermetallics | $Co_3Sn_2$, $Ni_3Sn_2$ |
| II-VI compounds | ZnS, $ZnS_{1-x}Se_x$, CaS, SrS, BaS, $SrS_{1-x}Se_x$ CdS, CdTe, ZnSe, ZnTe |
| Other chalcogenides | $Ge_2Sb_2Te_5$, GeTe, $Sb_2Te_3$, $Cu_{2-x}Se$, $In_2Se_3$, $Bi_2Se_3$, $Bi_2Te_3$, $TiS_2$, $MoS_2$, $ReS_2$, $ReSe_2$, $SnS_2$ |
| Fluorides | $MgF_2$, $CaF_2$, $LaF_3$, $YF_3$, LiF, $AlF_3$ |
| Carbonates/Phosphates | $Li_2CO_3$, $CaCO_3$, $Li_3PO_4$, $Al_xP_yO_z$, $Ti_xP_yO_z$ |
| Polymers | polyimide, MOF-5, IRMOF-8 |

# ALD research group at University of Helsinki

Funding during the past few years

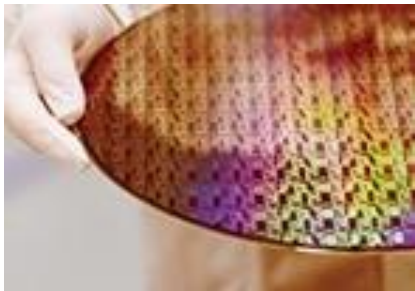
- Academy of Finland
- Finnish Funding Agency for Technology and Innovation (Tekes)
- European Union
- European Space Agency
- US Naval Research Global
- China Scholarship Council

- ASM Microchemistry (R&D unit located in the department building)

- Okmetic
- Picosun
- Beneq
- Murata (VTI Technologies)
- Elcogen
- AirLiquide
- Semiconductor Research Corp.
- Toyota Motors
- Samsung
- chemicals supplied by major ALD precursor companies
  SAFC Hitech, Air Liquide, ATMI, Praxair, Air Products, Honeywell, EpiValence

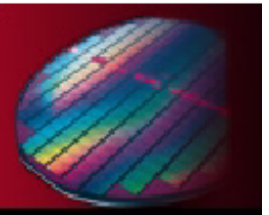
# ASM Microchemistry

- established in 1987 as Mikrokemia/Microchemistry Ltd, in Espoo, Finland, by Neste (later Fortum)
  - research on ALD for preparation of heterogeneous catalysts and solar cells
  - commercial ALD reactors since 1989
    - University of Helsinki buys its first in 1992
  - reorganized in 1997-8 to hold only the reactor manufacturing
- sold in 1999 to ASM International (the Netherlands), a globally operating semiconductor manufacturing tool supplier, renamed as ASM Microchemistry
  - moved to Kumpula in 2004



ASM
The Process of Innovation™

INNOVATION!
THAT'S ASM.



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**ASM International N.V. teams up with University of Helsinki for Atomic Layer Deposition Research; Restructures its ASM Microchemistry Operations**

BILTHOVEN, the Netherlands, August 25, 2003 --- ASM International N.V. (Nasdaq: ASMI and Euronext Stock Exchange in Amsterdam: ASM) announced today that it intends to enter into a long-term co-operative agreement with the University of Helsinki to jointly pursue further development of Atomic Layer Deposition (ALD) technology. As part of this agreement, ASM intends to relocate its Espoo, Finland, research and development activities to the nearby campus of the University of Helsinki, Finland.

**Major aspects of the collaboration agreement**

- **funding for 4 PhD students for five (+ five + five, renewed in 2008 and 2013) years: 60 researcher years by the end of 2018**
  - **IP transfer from university to ASM**
- **rental of lab space from the Chemistry department**
  - **converted to a clean room**
- **rental of office space**
- **cross-use of analytical instruments**

ALD
CoE
FINNISH CENTRE OF EXCELLENCE
IN
ATOMIC LAYER DEPOSITION
ASM

# ALD™ Technology Platform and Organization at ASM

ASM

Front-End Operations

PEALD

ASMGK (Korea)

Precursor Exploration
Concept and Feasibility
Materials R&D
Thin Film Characterisation

ALD

ASM Microchemistry (Finland)
(in the University of Helsinki)

ASM Belgium located at imec

Process Development
Process Integration 32 - 22 nm
(A412) Demo Lab 300 mm
Bilateral and IIAP Projects

Product Development,
Marketing and Support,
Final Mfg,…

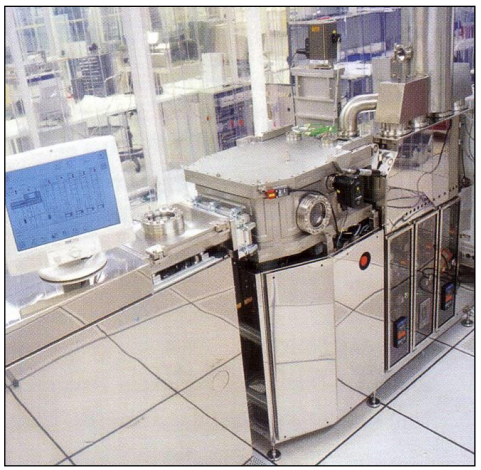
© 2009 ASM

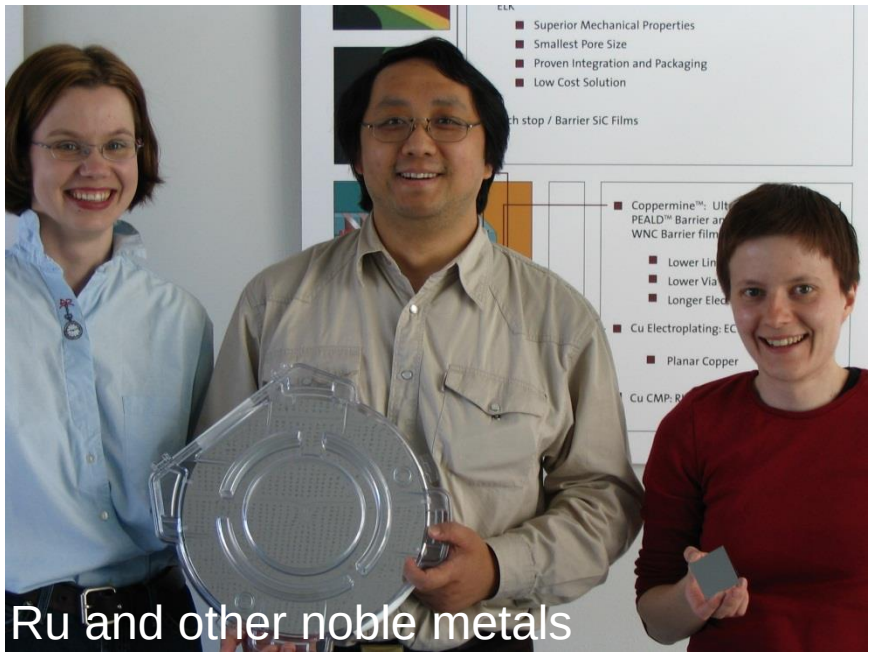
Suvi Haukka, June 2009

customers

# ALD research at University of Helsinki

- process development with smaller reactors of university
- scale-up to larger substrates at ASM Microchemistry

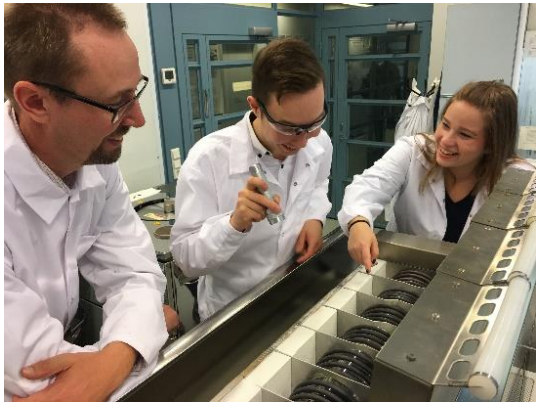


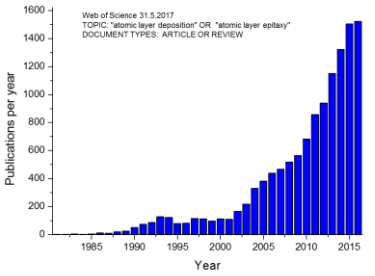


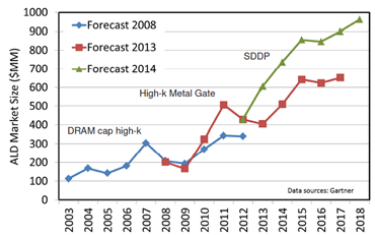
Ru and other noble metals

Petra Alén HY
Titta Aaltonen HY
Wei-Min Li ASM Microchemistry

# Conclusions






- ALD is a superior method for depositing the most advanced and challenging thin film materials
  - rapid growth both in academia and industry
- chemistry is the key for the success of ALD
- Helsinki ALD (Univ. Helsinki) has worked on ALD chemistry since 1990 and developed a great variety of new processes
- close collaboration with industry, ASM Microchemistry in particular but also with others, has enabled a combination of basic research and industrial relevancy in the most successful manner

# University of Helsinki alumni Wei-Min Li, CTO of Leadmicro

Jiangsu Leadmicro Nano-Equipment Technology Ltd
Xingshuo Rd9-6, New District, Wuxi, Jiangsu, P.R. China 214028