New Surface Properties by Atomic Layer Deposition

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HANNOVER MESSE MicroTechnology
Forum Innovations for Industry
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Turning Innovations into Success

Outline

- Company information
- ALD in short
- New surface properties enabled by ALD
  1. Ultra-high barrier films against moisture
  2. Artificial materials for optics
  3. Improved cracking resistance of glass
  4. Surface passivation of silicon wafers
  5. Nanoscale polishing of surfaces
  6. Metal-like decorative surfaces for plastics
- Industrial deposition equipment

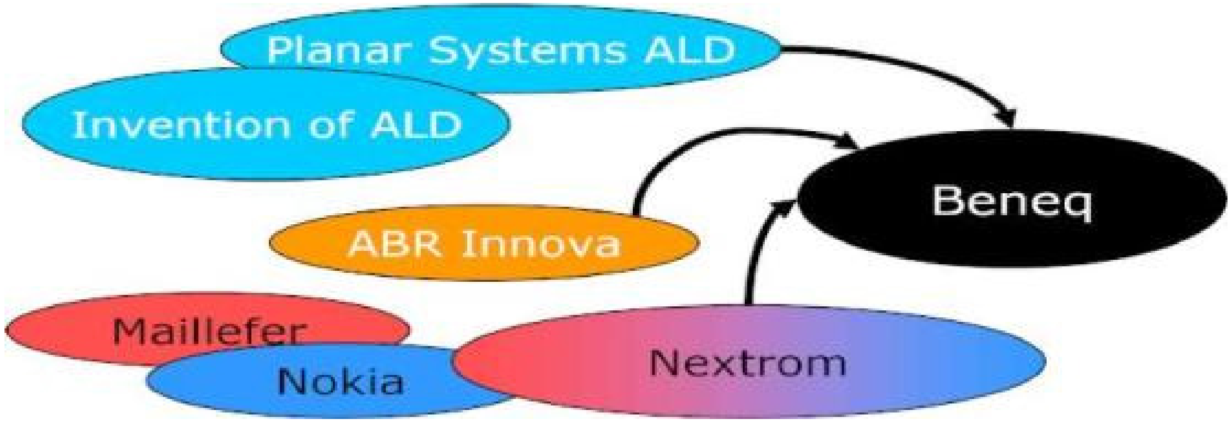
Company info

Established: 2005 by MBO spin out from Nextrom (ex. Nokia-Maillefer) to focus on functional coatings.

Ownership: Privately owned
Domicile: Vantaa, Finland

Products: Industrial and R&D equipment and technologies based on
- Aerosol coating (nHALO and nAERO)
- Atomic Layer Deposition (ALD)

Sales Offices: Germany, China, USA
+ representatives in several countries



Planar Systems ALD

Invention of ALD

ABR Innova

Beneq

Maillefer

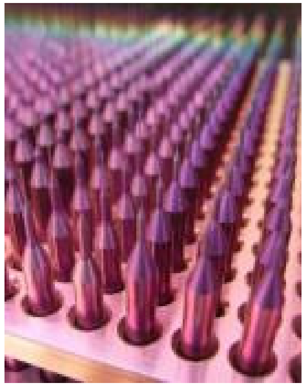
Nokia

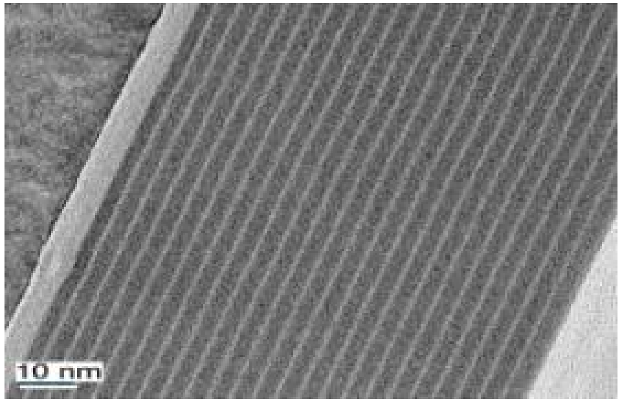
Nextrom

Markets and Applications

Beneq provides nano-technology enabled solutions for

- Cleantech and renewable energy; advanced thin film technology
- Glass industry; energy saving glass, easy-cleaning glass
- Medical industry; biocompatible thin film coatings
- Research and development; advanced coating tools
- Industrial thin film coatings





Solid ALD technology background

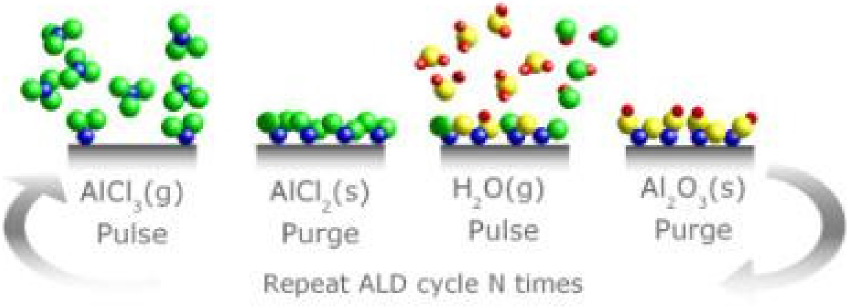
Beneq has:

- Cumulated experience of different ALD reactor generations over the past 30+ years
- Experience in global industrial production equipment market
- Over 1200 delivery projects
- Over 150 MCVD lines to R&D and industry
- Delivered almost 100 installed ALD systems

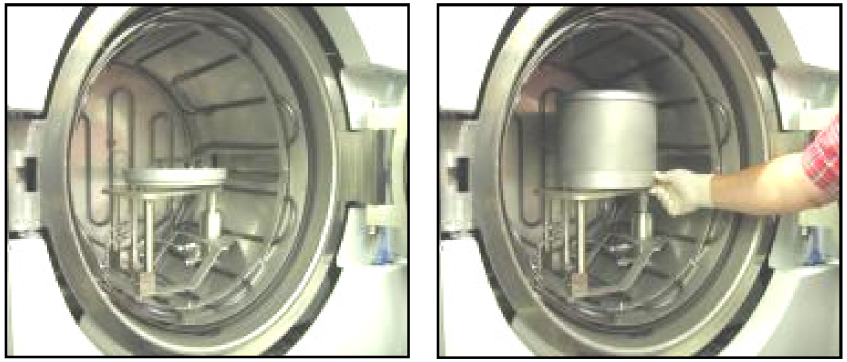
ALD in short

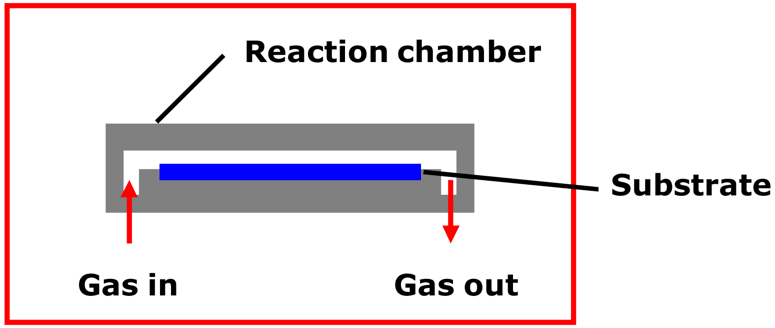
Chemical vapor deposition based on saturating surface reactions

- Typically two precursor chemicals
- Inert carrier gas, typically at 1 mbar
- Surface controlled, self-limiting film growth



- Thin Film Electroluminescent Displays (TFEL) was the main ALD application for the first 25 years
- Semiconductor industry found ALD during 90´s
- Intel's production for gate oxide started in December 2007
- Fastest processors, memory devices and hard disks are enabled by ALD





Strengths of ALD

1. **Extreme surface conformality –** The best technology to deposit conformal films; nanotubes, nanowires, diffractive optics, DRAM, 3D parts
2. **Pinhole free films –** “Bottom up” growth of ALD is naturally pinhole free; excellent for passivation, barriers and insulators
3. **Repeatability, precision –** Easy to implement in production; demanding batch processes for TFEL, optics, complex parts; without feedback or tuning; identification, decorative
4. **Thin, dense, smooth films <2nm –** Films formed one atomic layer at a time; gate oxides, HDD
5. **Artificial materials –** Digital control of ALD provides a way to create artificial materials; a critical benefit in many innovative R&D applications

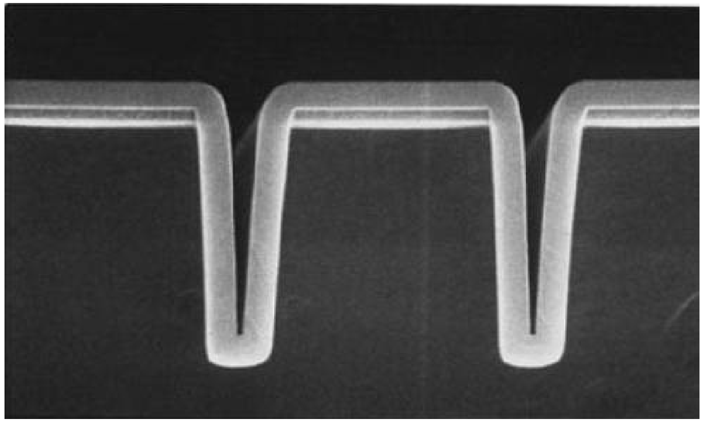
ALD Features - Conformality

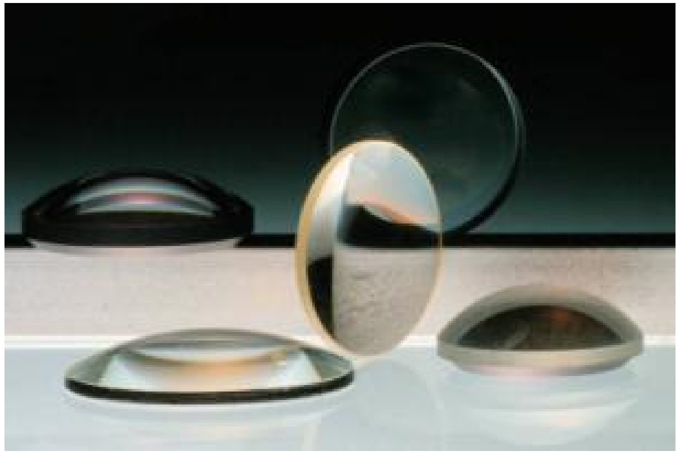
Put films to places where others can not.

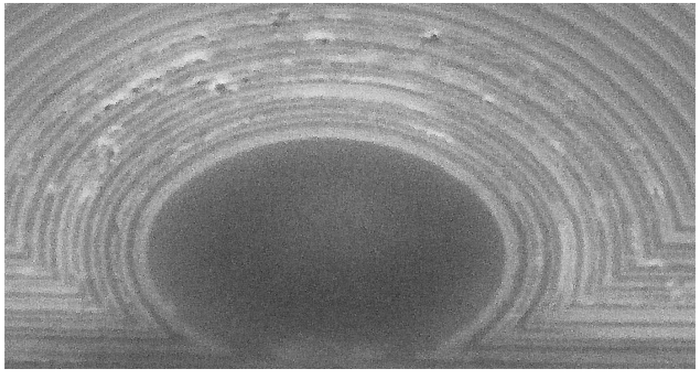
Examples: Semicon memory trenches, Mechanical part passivation barriers.

ALD is the best technology to deposit conformal films. 3D part coating.

Inside tubes and holes, pores, on particles, inside sintered materials







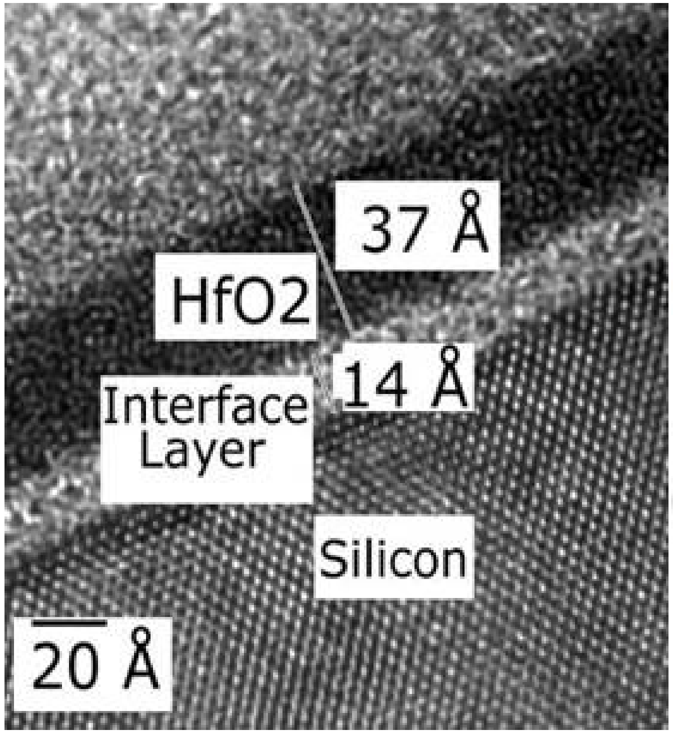
ALD Features - Thin, precise, dense

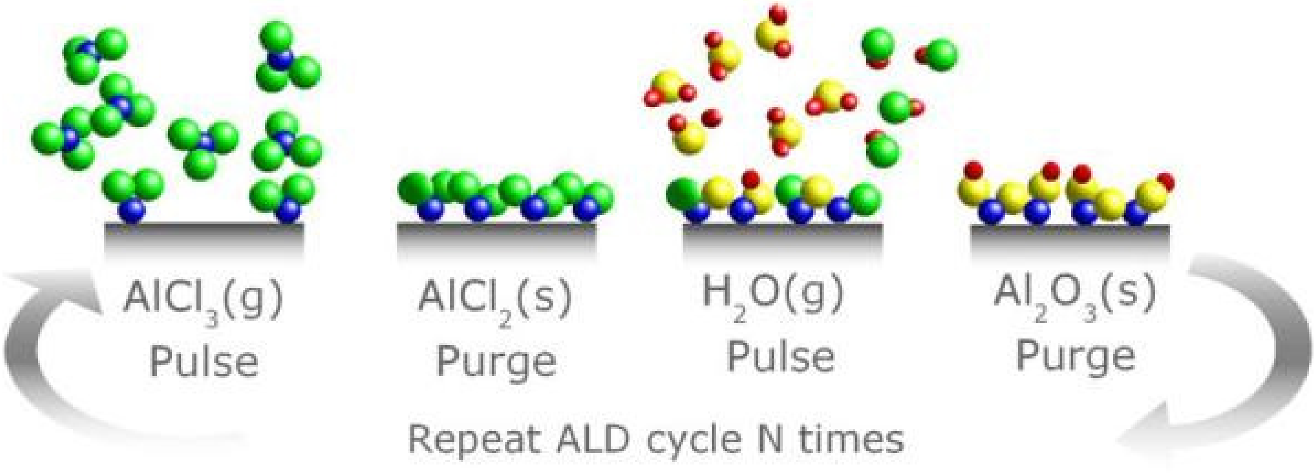
Resolution 0.3 … 11 Å depending on material.

Examples: Transistor gate oxide, optical films

Film is formed one molecular layer at a time, the material packs as tight as it can, at that temperature.

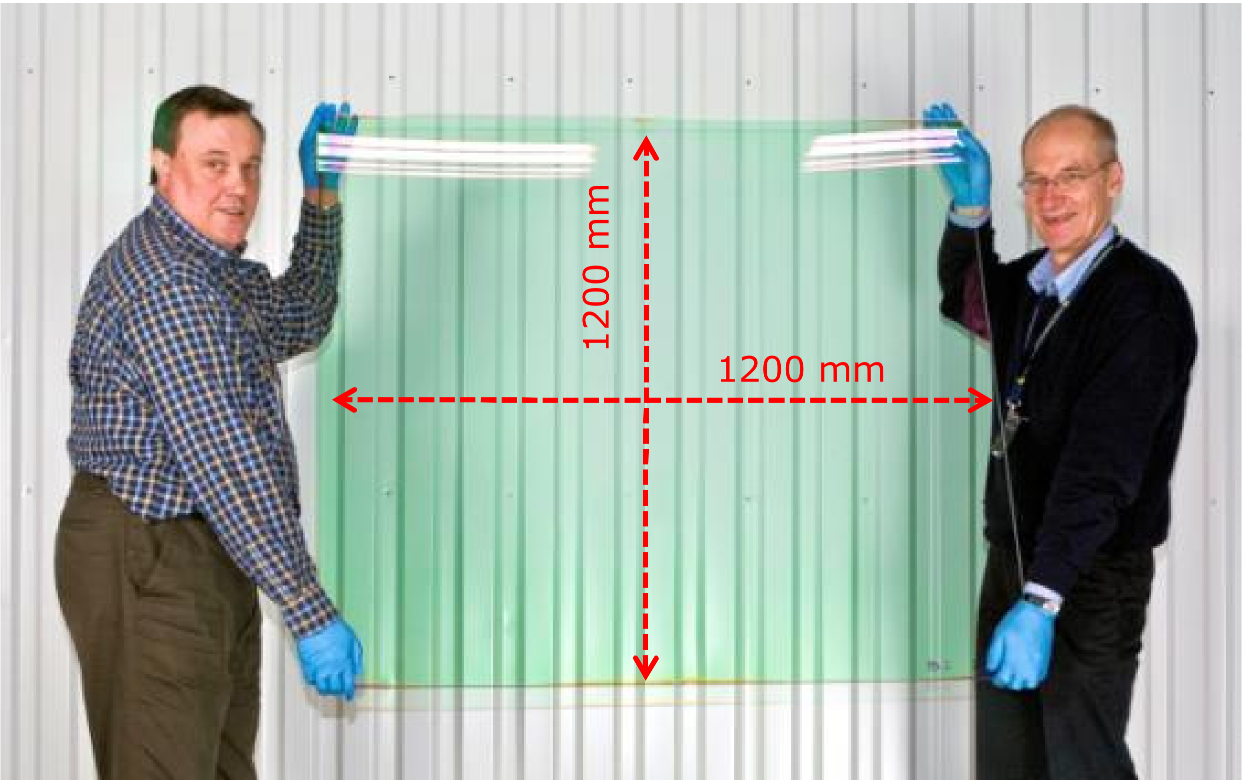
PVD methods rely on added energy to provide comparable density. In general, the more added energy, the more added stress.





Industrial large scale applications

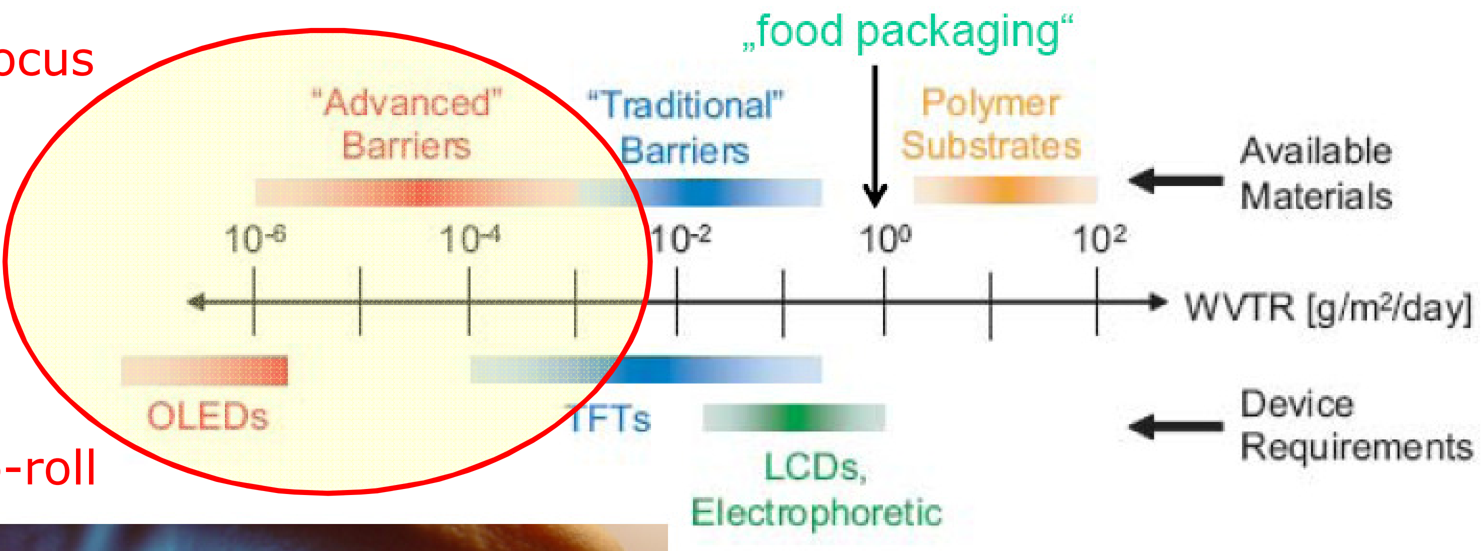
Beneq focus is in large scale industrial coating applications



Beneq has delivered world record size industrial in-line ALD coating system for thin film photovoltaic applications

Ultra-high barrier films against moisture

Advanced moisture barrier applications



Beneq focus

Also roll-to-roll

Conventional glass-lid encapsulation:

→ not flexible

→ expensive

→ problematic for transparent OLEDs

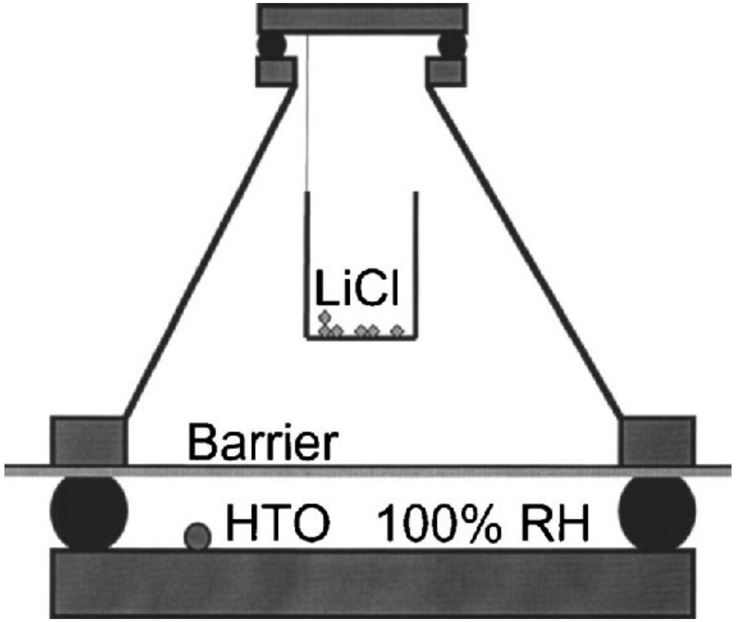
efficient thin-film encapsulation needed

From presentation by Thomas Riedl, Institute of High-Frequency Technology, Technical University of Braunschweig

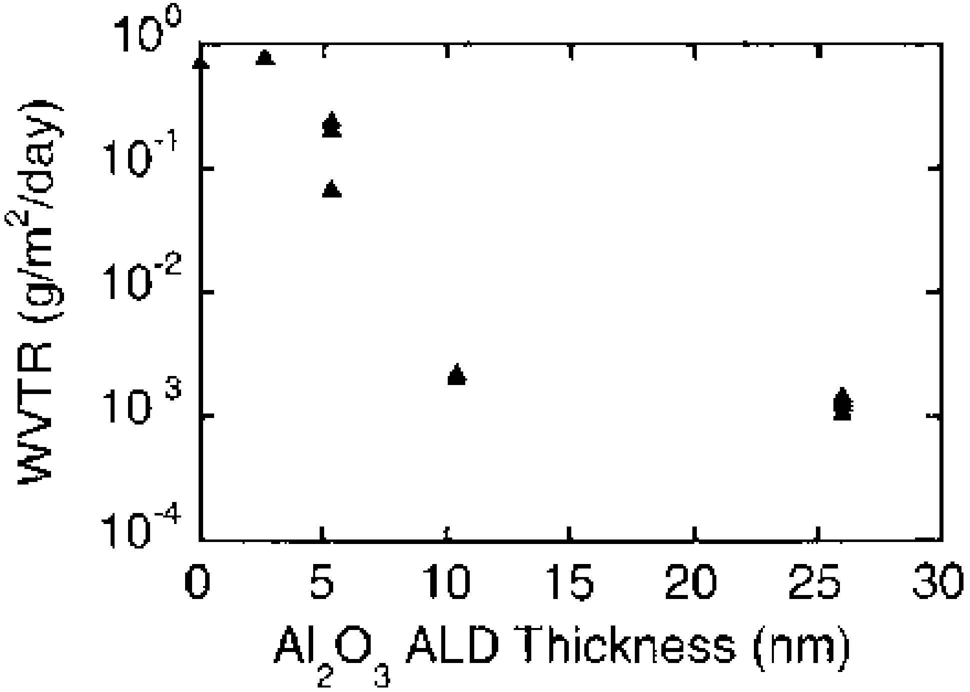
ALD for moisture barrier applications

Coatings for flexible electronics – displays, RFID, sensors, …

- Encapsulation/barrier layer on top of the device structure
- Barrier layer on plastic substrate



Tritiated (HTO) water test



Water vapor transmission rates (WVTR) vs. thickness of ALD Al2O3 films grown at 120 C on PEN

M.D. Groner, et al., Gas diffusion barriers on polymers using Al2O3 atomic layer deposition, Appl. Phys. Lett., **88**, 051907 (2006)

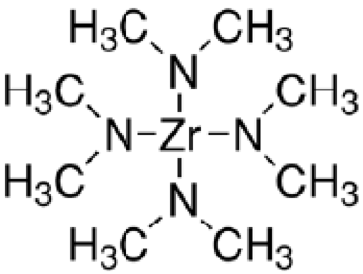
Stacked Al_2O_3/ZrO_2 ALD nanolaminate

Next generation thin film encapsulationn → Nano-laminates

cyclic deposition of Al_2O_3 and ZrO_2

20 cycles Al_2O_3 (2 nm)
20 cycles ZrO_2 (3.8 nm)

Precursor for ZrO_2 preparation



Tetrakis(dimethylamido)zirconium(IV)

TDMA(Zr) heated to 75 °C

Aim:

- → increased film density
- → forced amorphicity
- → avoid permeation channels

Adv. Mater. (in preparation)

From Presentation by Thomas Riedl, Institute of High-Frequency Technology, Technical University of Braunschweig

Permeation rates of Al_2O_3/ZrO_2 ALD nano laminates

Test conditions (climate cabinet): 70 °C and 70 % RH

encapsulation	permeation rate for water (g/m² day)	permeation rate for oxygen (cm³/m² day)
Al_2O_3 100 nm @ 80 °C	3.4×10^{-4}	1.5×10^{-1}
Al_2O_3 & ZrO_2 100 nm @ 80 °C	6.6×10^{-5}	2.9×10^{-2}
Al_2O_3 130 nm @ 80 °C	8.8×10^{-5}	3.9×10^{-2}
Al_2O_3 & ZrO_2 130 nm @ 80 °C	4.7×10^{-5}	2.1×10^{-2}

with $E_a = 92$ kJ/mol → 5×10^{-7} (at RT)

Adv. Mater. (in preparation)

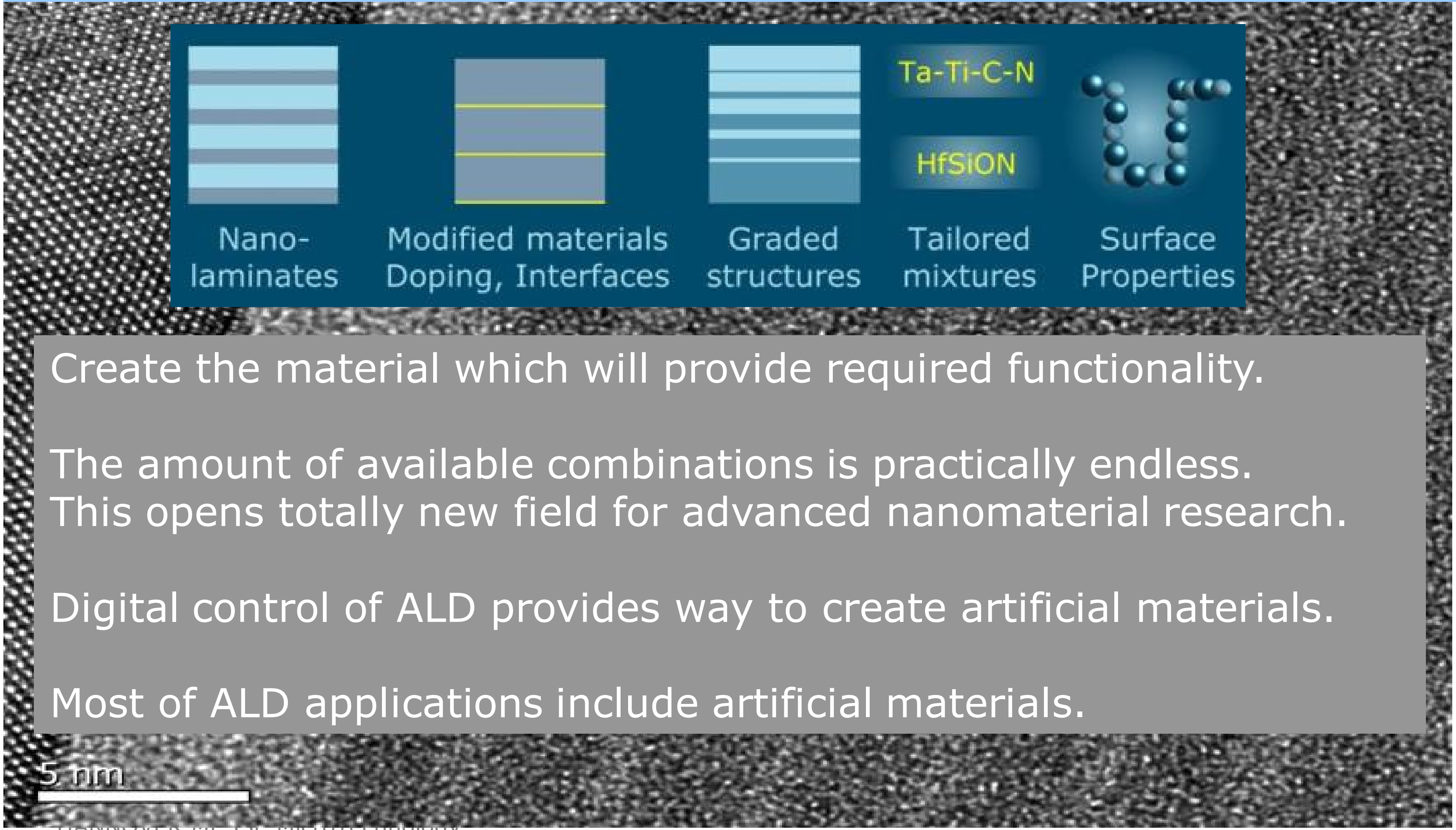
From Presentation by Thomas Riedl, Institute of High-Frequency Technology, Technical University of Braunschweig

Artificial materials by ALD

ALD Features - Artificial materials

New materials are often built, not discovered.

Examples: Transistor gate oxide, optical materials, ATO insulator / transparent electronics



Create the material which will provide required functionality.

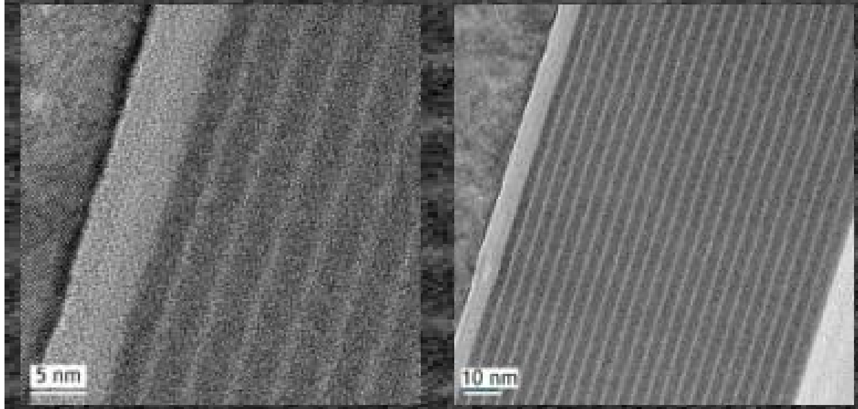
The amount of available combinations is practically endless.
This opens totally new field for advanced nanomaterial research.

Digital control of ALD provides way to create artificial materials.

Most of ALD applications include artificial materials.

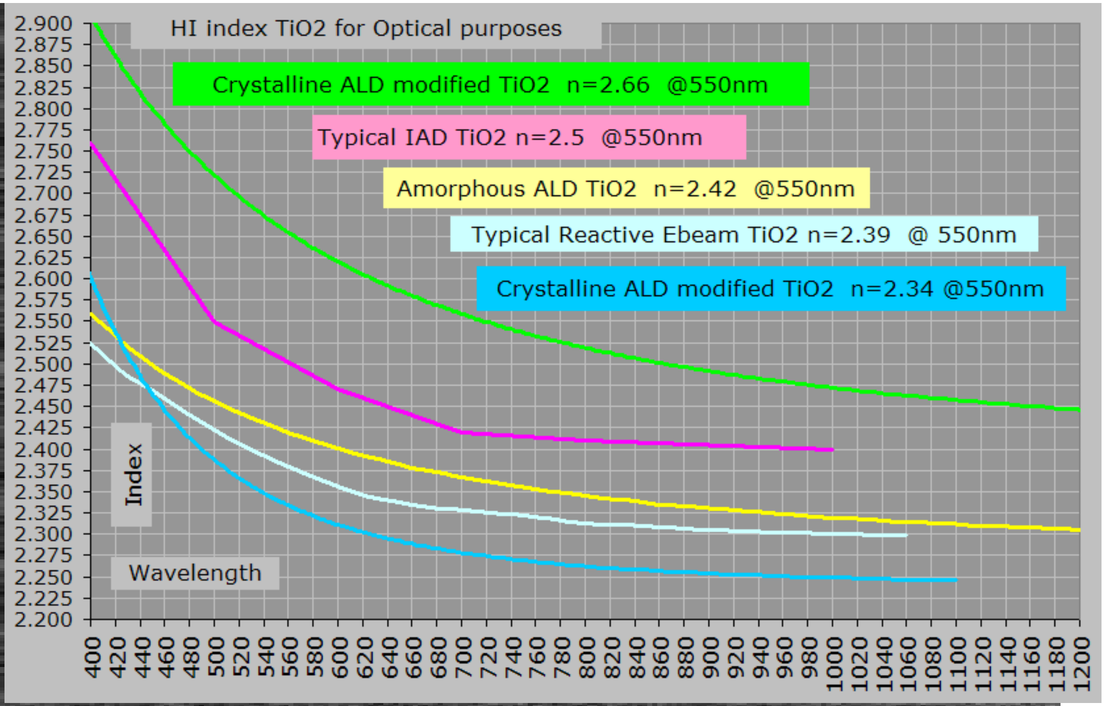
ALD Optics - Artificial materials

Modified TiO2 High Index material



HR TEM Pictures by courtesy of E. Kauppinen and H. Jiang, HUT, Finland

From the left: Si wafer - Interface- Layered High Index film material



- ❑ For visible and IR range the HI index material is TiO2
  - Typical Reactive E-beam TiO2 n=2.39 @ 550 nm
  - Amorphous ALD TiO2 n=2.42 @ 550 nm
  - Typical IAD TiO2 n=2.5 @ 550 nm
  - Crystalline ALD modified TiO2 n=2.67 @ 550 nm (Crystalline material is modified to appear as optically amorphous. Very useful optical material. Ref: Patent EP1674890)

Note: Index values depend on the process.

Improved cracking resistance of glass

Background

- Thinner and thinner glasses (even 0.03mm) are requested for displays, IRCFs, MEMS
- Difficulties in glass handling due to the stresses caused by one-side coating and cracking of the substrates.
- Griffith flaws are 10-100Å flaws on brittle material surface[1,2]
- A Griffith flaw acts as a point-of-origin stress concentrator to initiate a crack.
- Initiated cracks can propagate under certain conditions

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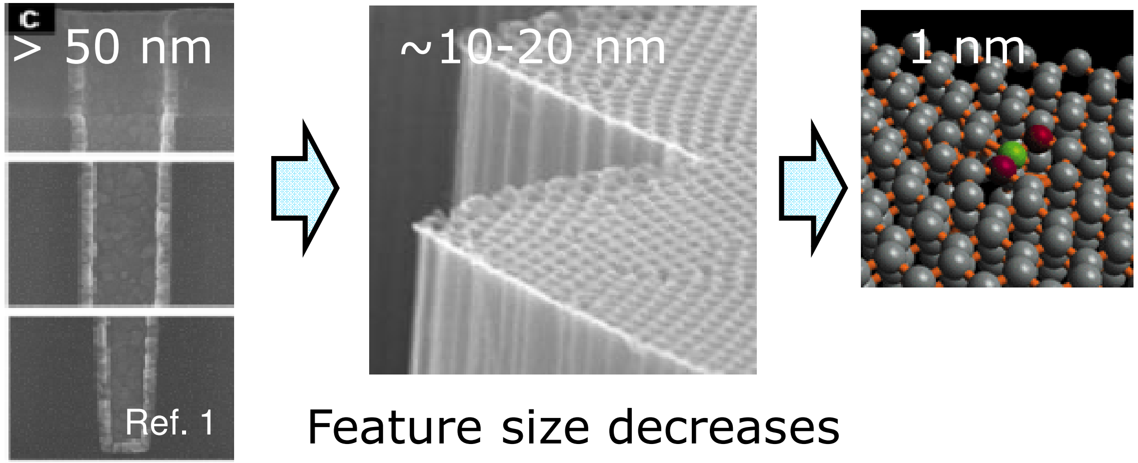
[1] A.A. Griffith, R. Soc. Phil.Trans. A221 (1920) 163.
[2] B. Sugarman, J. Mat. Sci. 2 (1967) 275.

Suggested mechanism

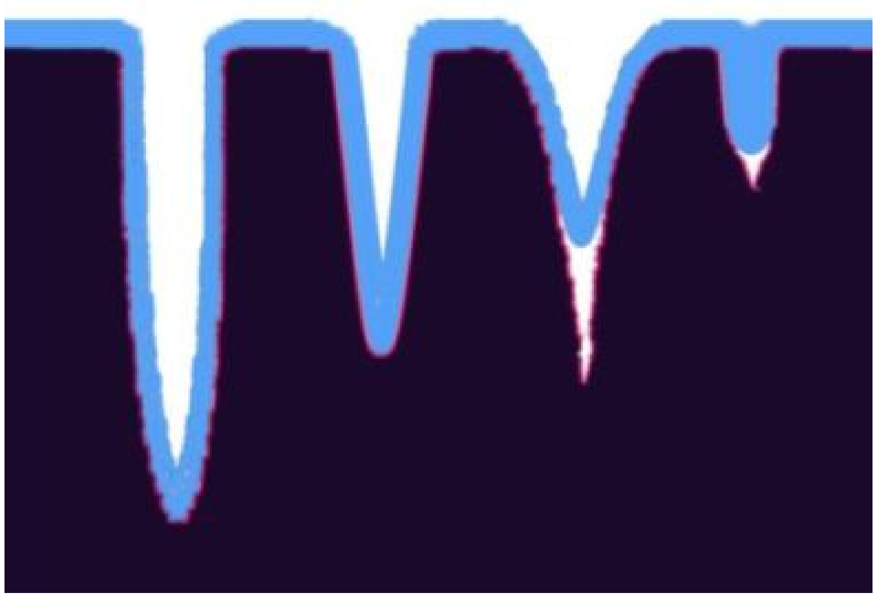


Feature size decreases

[1] Niinistö et.al., Chem. Mater. 19 (2007) 3319

$$\sigma_r = \frac{\sigma\sqrt{\pi a}}{\sqrt{2\pi r}}$$

σ = subjected tension
σ_r = stress at the crack tip
a = crack length
r = crack tip radius



- Crack tip radius will increase
- Decreased local stress at the crack tip

→ Cracking resistance increases

Optimisation of the ALD process

- Large batch optimisation for uniform coating
- With 288 pcs of 100 x 100 mm^2 substrates non-uniformity less than 2% using cycle time < 3s.

Beneq P400A reaction chamber with a stack of 100 x 100 mm^2 glass substrates.

4- point bending results

	Soda lime glass	20 nm Al_2O_3	16 nm SiO_2
S_{mean}	125.21	143.02	152.45
S_{median}	126.53	137.53	157.76
S_{dev}	12.04	19.2	17.65
Weib	4.7	4.7	11.02
$Weib_{corr}$	4.57	4.57	10.72

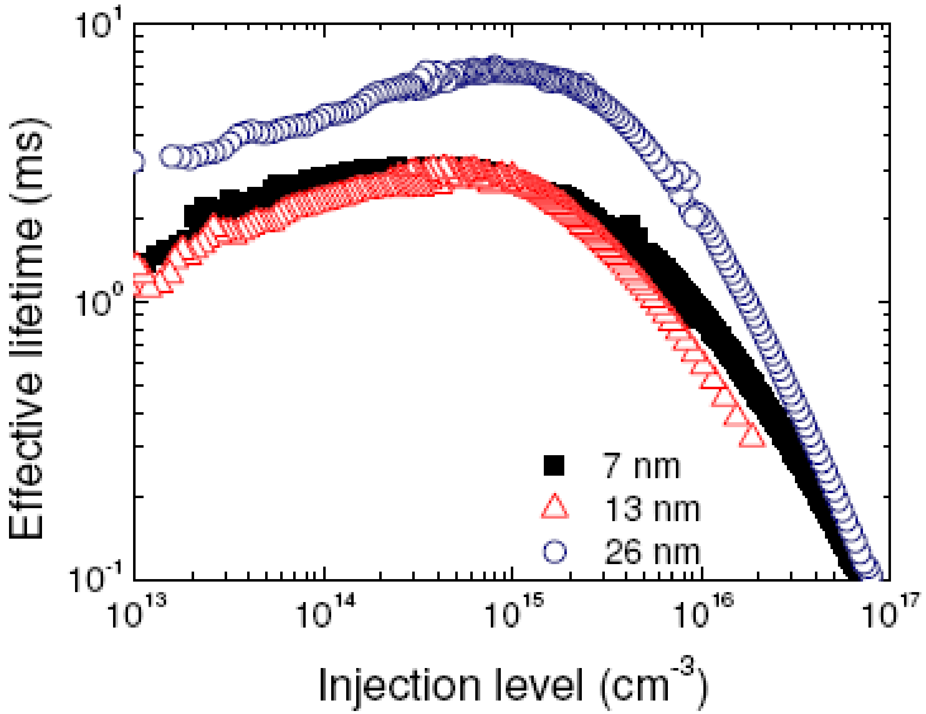
- Both Al_2O_3 and SiO_2 increased the cracking resistance of thin glass
- SiO_2 increased also the Weibull modulus

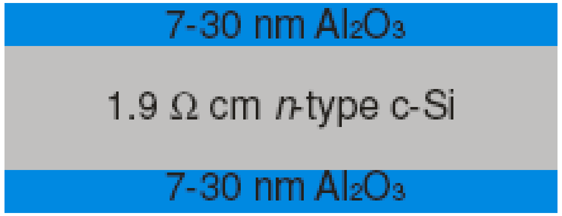
Measured values of

- ❑ S_{mean} - mean value of flexural strength (MPa),
- ❑ S_{median} – median value of flexural strength (MPa)
- ❑ S_{dev} – standard deviation of flexural strength (MPa),
- ❑ Weib – Weibull modulus (max. likelihood)
- ❑ $Weib_{corr}$ – corrected Weibull modulus

Surface passivation of silicon wafers

n-type Si Surface Passivation by ALD-Al2O3





7-30 nm Al_2O_3

1.9 Ω cm *n*-type c-Si

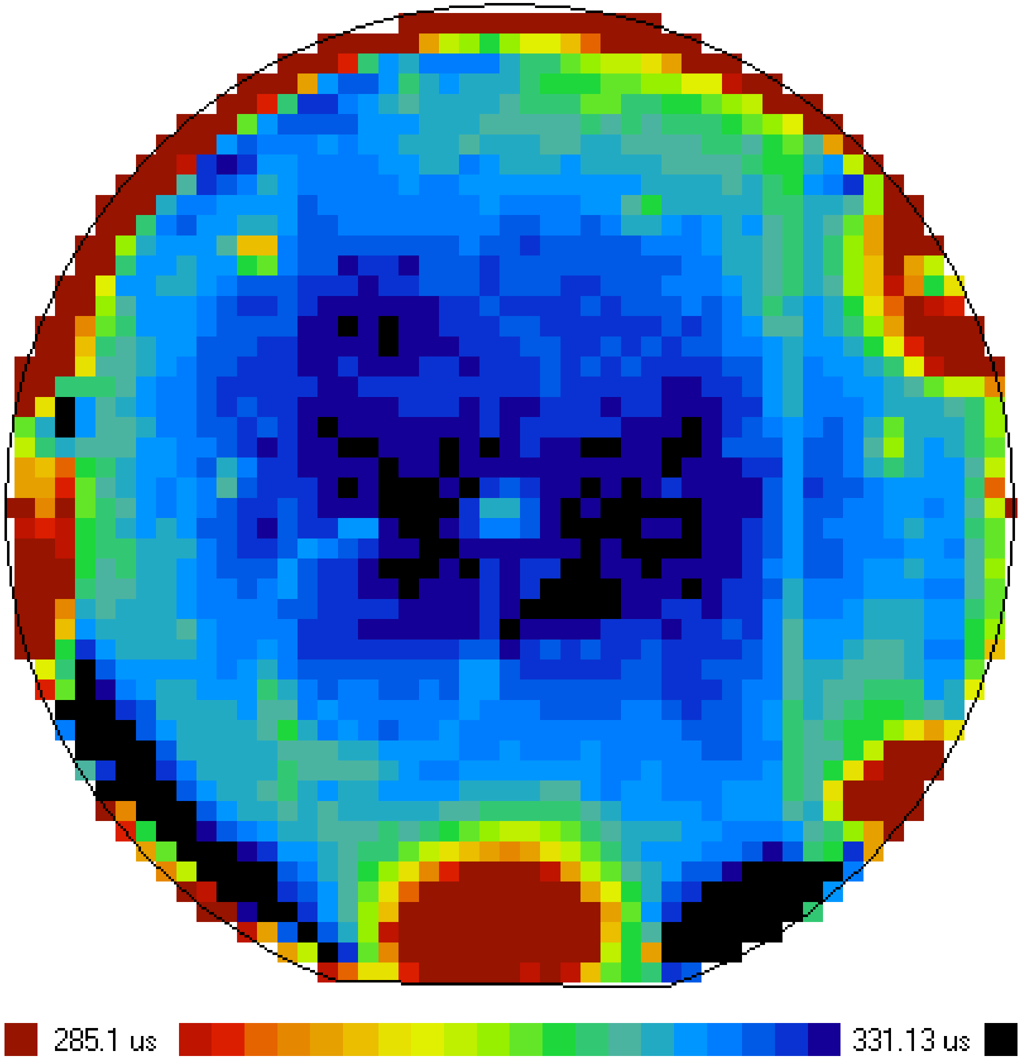
7-30 nm Al_2O_3

- **Effective lifetime in excess of 6 ms measured ($S_{eff} \leq 2$ cm/s)**
- **7 nm Al_2O_3 film still yields $S_{eff} \leq 4$ cm/s**
- **Effective lifetime slightly decreases for decreasing injection level**

Hoex et al., Appl. Phys. Lett. 89, 041202 (2006)

Uniformity of Lifetime Map over 4” Wafer

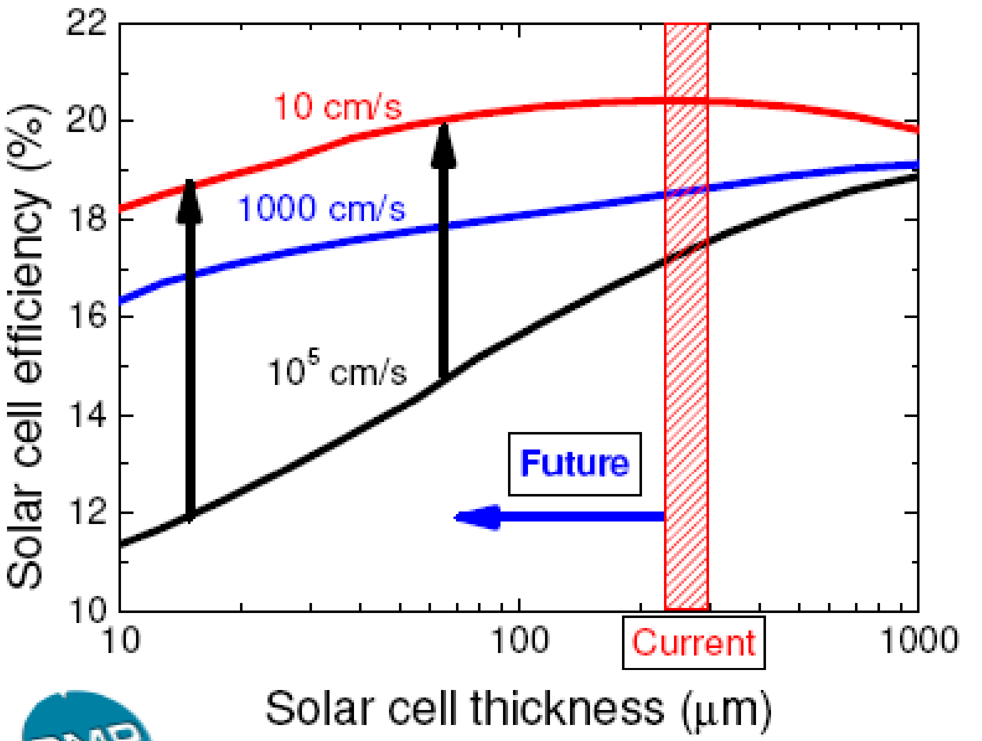
Double side thermal ALD Al2O3 coated 2 ohm.cm <111> p-type 4” wafer



Uniform lifetime of charge carriers

Back surface passivation for efficiency

- Surface passivation on the back is essential when decreasing solar cell thickness
- Current technology (Al BSF) yields only ~1000 cm/s on the back side!



Hoex et al., Applied Phys. Letters **89**, 041202 (2006)

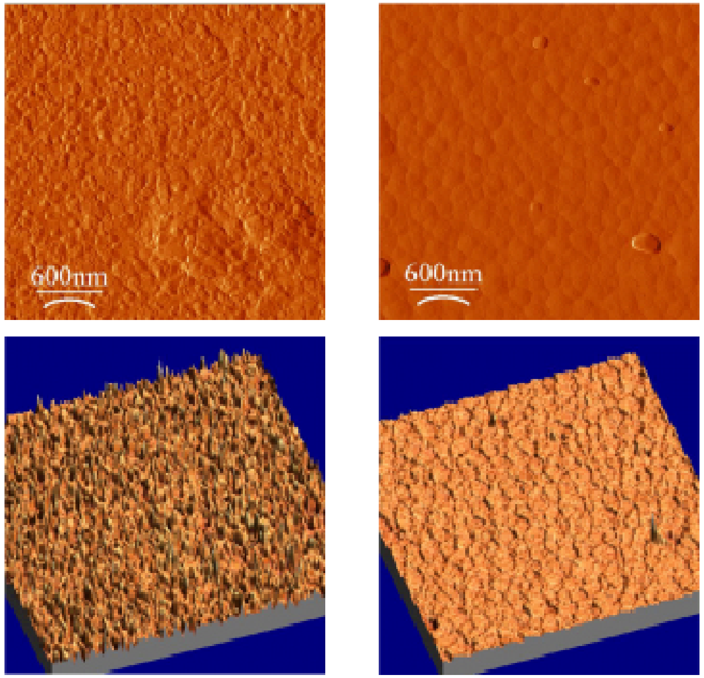
Improved cell efficiency by 1…2 %-units!!

Nanoscale polishing of surfaces

Smoothening effect by ALD

	RMS* nm 1.0µm x 1.0µm	Max. Peek to Valley Z[nm]/1.36 µm 1.0µm x 1.0µm
Rough surface**	0.62	3.80
Rough surface + 20nm ALD layer	0.45	1.96
Rough surface + 200 nm ALD layer	0.28-0.34	1.52-1.56

Measured with AFM
**Rough surface is polycrystalline TiO2 on glass



Rough surface

Rough surface +
200nm smoothening coating

Planarization – nanoscale polishing

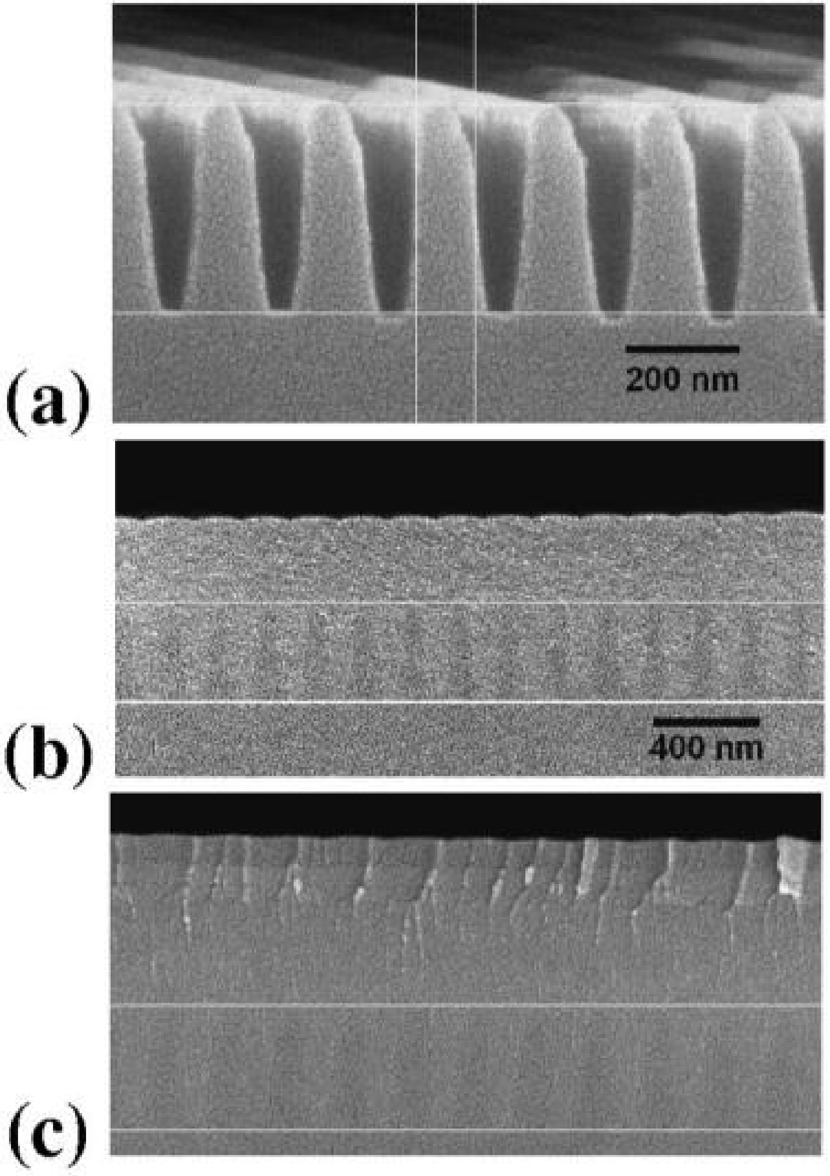
- Trench filling of diffractive optics utilizing conformality of the ALD
- ALD provides an excellent solution by first filling the trench and then planarizing the surface.

(a) Nanograting prior to filling

(b) ALD was used to fill the grating

(c) Complete optical retarder with the top antireflective coating layers deposited by ALD as well

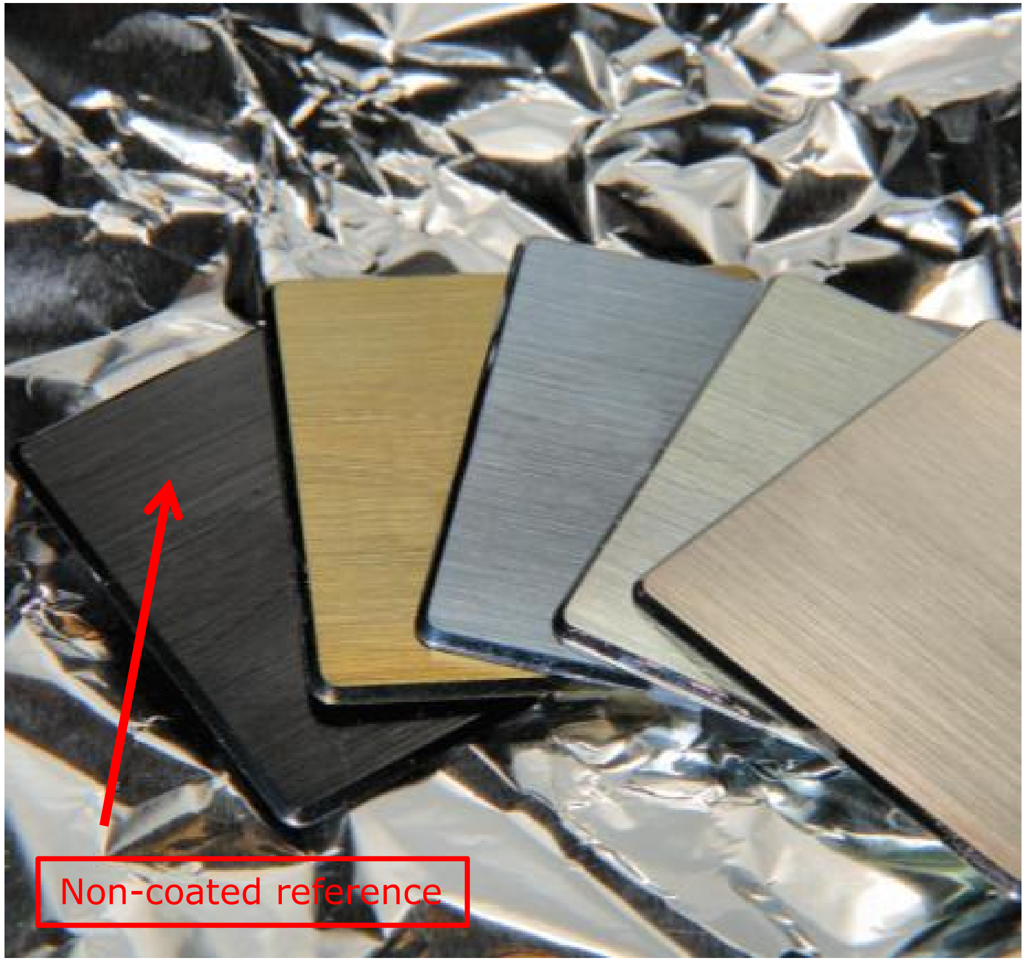
Also for planarizing substrates such as OLEDs



OPTICS LETTERS / Vol. 30, No. 14 / July 15, 2005 Wang et al.

Metal-like decorative surfaces for plastics with ALD

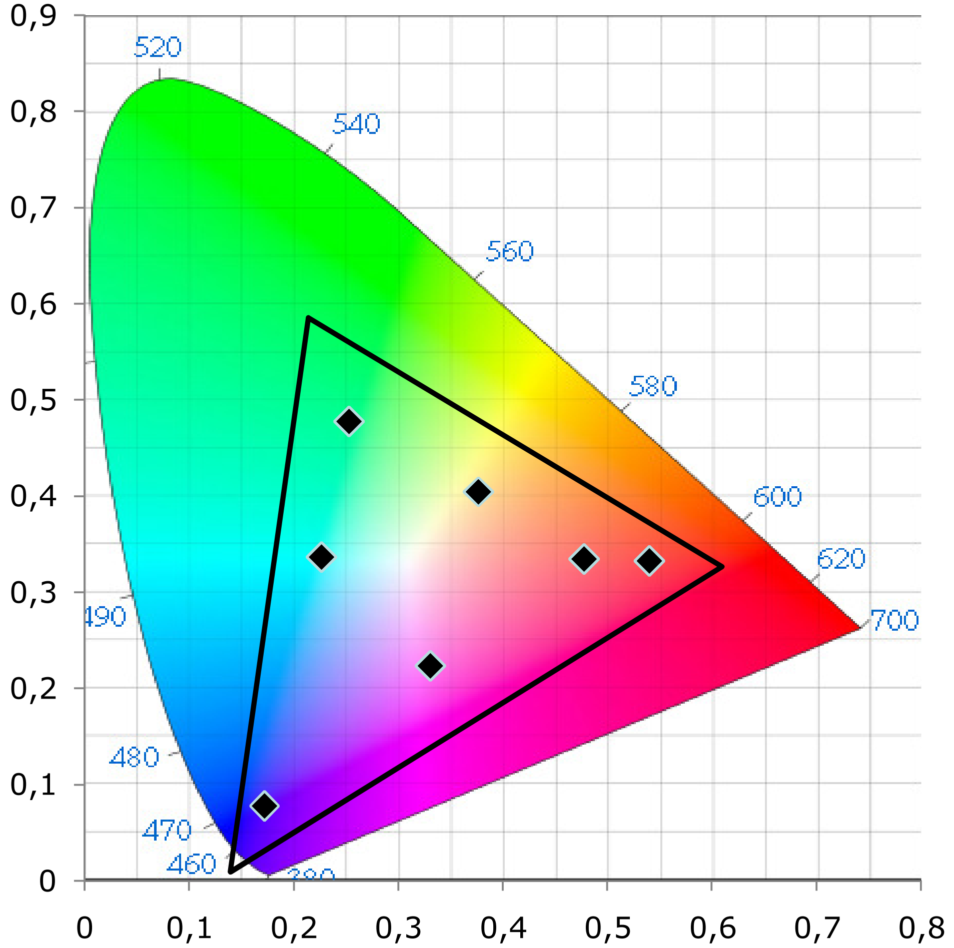
Metal-like surfaces on plastics



Examples of decorative metal-like coatings on plastics. The leftmost black piece is the non-coated reference.

- Metal-like surface decorations on plastics based on dielectric mirror
- RF compliant coating (100% non-metallic)
- Very wide colour palette (colours imitating gold, silver, steel, bronze, titania...)
- Low processing temperatures suitable for wide range of plastics
- Coatings made on large scale batch processes
- Suitable also on elastomers, silicon and metals

Countless metal-like coating colour options



- Colour examples shown are in the coating thickness range of 186...356 nm
- Highly repeatable colour from batch to batch

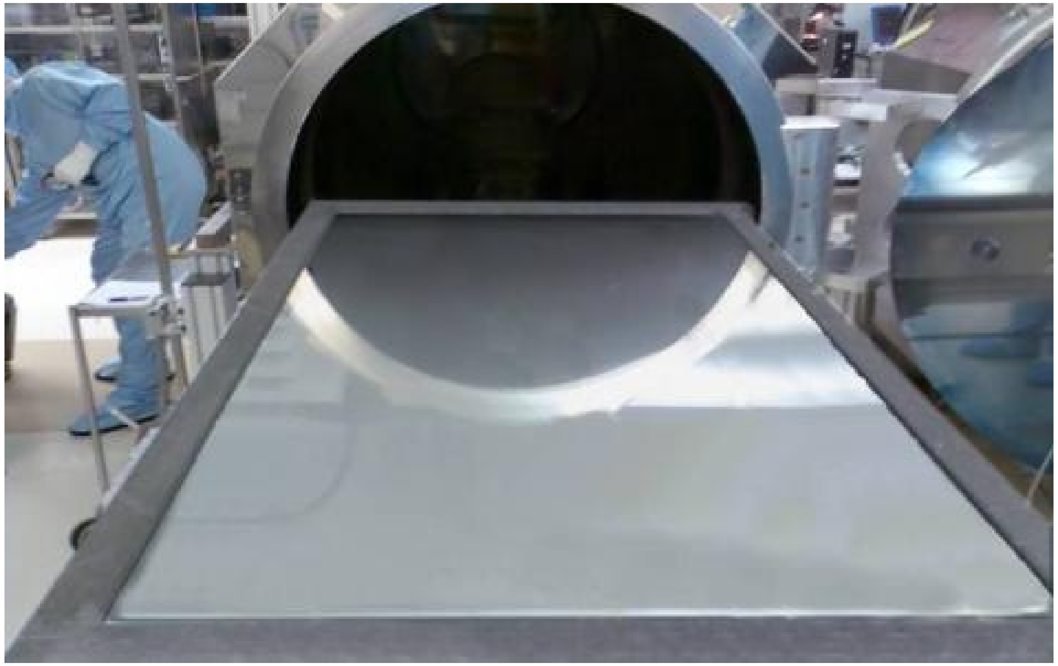
Equipment offering

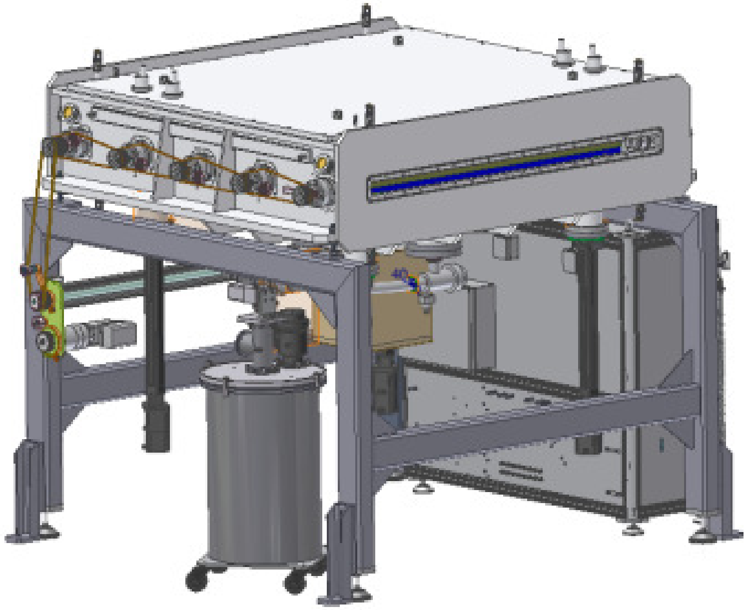
ALD equipment and technology

Equipment range:

- **TFS 200** – Thermal/plasma ALD tool for R&D purposes
- **TFS 500** – Thermal/plasma ALD equipment for batch production
- **TFS 4x300** – Batch ALD equipment for PV
- **TFS 1200** – In-line ALD equipment for PV
- **TFS 2x325** and **TFS 4x750** – ALD equipment for displays
- **P400A, P800** – ALD equipment for manufacturing

Industrial scale reaction chambers





In-line TFS 1200 (2x600x1200 mm^2)

Reactor chambers for *e.g.* PV applications, 600x1200 mm^2 substrates

Reactor chamber for optical applications (bandpass filter), >8 m^2/batch

TFS 200 ALD tool for research

Thermal and plasma-assisted ALD

Reaction chambers		
Wafer	200 x 5mm (∅ x H)	
3D / batch	200 x 100mm (∅ x H)	
Powder	70 x 80mm (∅ x H)	
Precursor sources	max.	8 gas 3 liquid 4 hot
Process temperature	max. 500° C	
L x W x H	1200 x 600 x 1200 mm	
Control system	PLC + PC (HMI, WinXP)	

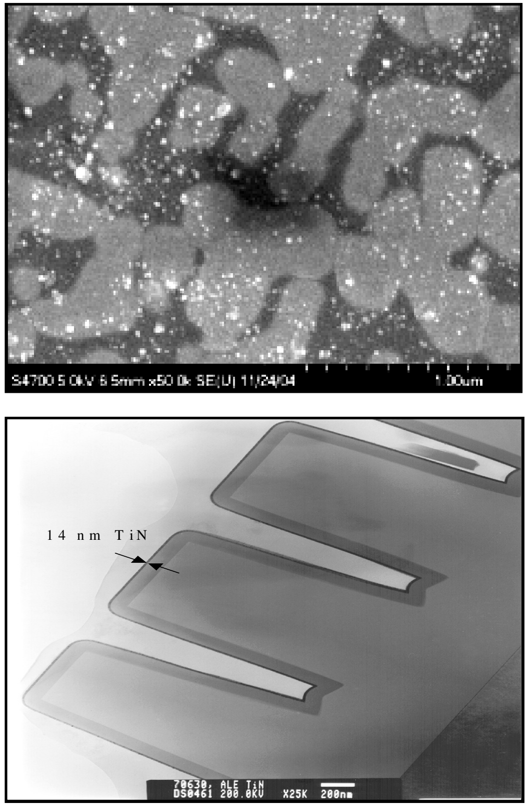
Customized production ALD equipment

- Tailored versions of TFS 500, P400A, P800, TFS 2x325, TFS 4x750 and TFS 1200 ALD equipment
- Large batch coating equipment
- In-line equipment, also integrated modules as a part of larger setup
- Roll-to-roll coating equipment
- Substrate/part handling and transfer systems to integrate the ALD process to the other process steps

Pilot scale production & coating service

Beneq coating service facility in Espoo, Finland

Turning Innovations into Success



Application specific coating and material development services;

Verification and pilot production services

Coating equipment

Thank you!

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