

Functional Surfaces

Atomic Layer Deposition for Thin Film Research and New Emerging Applications

Turning Innovations into Success



Outline

- Beneq
- □ Thin Film market outlook
- Atomic Layer Deposition (ALD) Technology
- ALD New Applications
- □ ALD in Photovoltaics
- Beneq ALD Systems for Industry and Research
- Turning Innovations into Success

Beneq Oy P.O.Box 262 Ensimmäinen savu FI-01510 Vantaa Finland.

E-mail: mikko.saikkonen@beneq.com



- **Established:** 2005 MBO spin out from Nextrom (ex. Nokia-Maillefer) with focus on Equipment and Technology for Functional Surfaces.
- Ownership:Privately ownedDomicile:Vantaa, Finland

Products: Industrial and R&D Equipment for coatings based on

- Atomic Layer Deposition (ALD)
- atmospheric pressure Aerosol Technologies

Sales Offices: Germany (Europe), China, USA; representatives and customer support globally











Thin Film Enabled Industries

Market by sector 2008-2018



Market growth of thin film enabled industries. Source: IDTechEx, Dresden, April, 2008







ALD Development History





Examples of IC Applications

- Gate oxide
- Barrier layers
- Primer layers
- Gate electrode

Examples of non-IC Applications

- Sensors
- Flat Panel Displays
- Solar panels
- Magnetic heads
- Memories
- Fuel cells





ALD Process

Process features: 0.1-5 mbar Pressure Temperature 60-500°C Gas flow 0.3-1.0 SLM **Reaction chamber** Substrate Vacuum chamber Gas in Gas out



Sequential process 1. A(g) Introduction of A(g) onto the substrate surface Chemisorption 11 . **Saturation** A(s) Formation of an A(s) monolayer surface Purge 11 . B(g) Introduction of B(g) onto A(s) surface Chemisorption IV. Formation of B(s) monolayer surface B(s) **Saturation** Purge

Surface controlled growth



$2 \operatorname{AICl}_{3}(g) + 3 \operatorname{H}_{2}O(g) \rightarrow \operatorname{AI}_{2}O_{3}(s) + 6 \operatorname{HCl}(g)$









CVD	ALD	PVD
Analog (µm/min) High growth rate	Digital (Å/cycle) High accuracy and repeatability	Analog (µm/min) High growth rate
Plenty of different materials	Oxides, nitrides, doped layers	Plenty of different materials including metals
Process parameter controlled	Surface controlled	Process parameter controlled Substrate movements
Mixable source materials	Highly reactive source materials	Physical transportation of the film material
Process parameter accuracy important	Flow dynamics important	High vacuum Process parameter accuracy important
Pieces with large surfaces 2-D surfaces	Pieces with large surfaces 3-D pieces Mixed structures	Small size pieces



Overview of ALD Materials

					8898	the	pure ele	ment ha	s been gr	own							
1	r	co	mpounds	with O	$\parallel \sim$		374										18
Ĥ			maguada	ith N	=	Z		other		da							He
ाच	2	CO	mpounds	s with IN				otherd	compoun	JS		13	14	15	16	17	пе
3	4	co	mpounds	with S				compo	ounds wit	n Te		5	6	7	8	9	10
Li	Be		mpounde		1993		1	- oompe				В		Ň	ŏ	F	Ne
	20						compour	nds with	Se				×				110
11	12					0.05.05.01	5.500 F (5.70		1010			13	14	15	16	17	18
Na	Ma											AI	14 Si	Р	S	CI	Ar
	Mg	3	4	5	6	7	8	9	10	11	12						
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34 Se	35	36
ĸ	Са	Sc	Ti	V	Cr	Mn	26 Fe	Co	Ni	29 Cu	Zn	Ga	Ge	As	Se	Br	Kr
1.							2000										5-20-010-0
37	38	39	40	41	42 Mo	43	44 Ru	45	46 Pd	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	52 Te	1	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ва	La*	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	TL	Pb	Bi	Po	At	Rn
87	88	89	104	105	106	107	108	109	110	111	-						
Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	February 2005						
85		5		8			89	5	12								
			58	59	60	61	62	63	64	65	66	67	68	69	70	71	T
La	anthan	oids*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
			90	91	92	93	94	95	96	97	98	99	100	101	102	103	- 5%
	Actino	ids**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

Figure 3: Overview of the materials grown by ALD. Classification according to Reactant A, with details of the investigations in Table III. Growth of pure elements as well as compounds with oxygen, nitrogen, sulphur, selenium, tellurium, and other compounds grouped together are indicated through shadings of different types at different positions. The elements are named according to the recommendations of The International Union of Pure and Applied Chemistry (IUPAC, http://www.iupac.org/reports/periodic_table/, dated 1 November 2004).

Ref. Riikka L. Puurunen J. Appl. Phys. 97 (2005) 121301-1 : Surface chemistry of atomic layer deposition: a case study for the trimethylaluminum/water process



- Oxides: Al2O3, TiO2, Ta2O5, Nb2O5, ZrO2, HfO2, SiO2(Al), SnO2, In2O3, ZnO, MgO, La2O3, Y2O3, CeO2, Sc2O3, Cr2O3, SrO, Er2O3, VO2, B2O3, Co2O3, CuO, Fe2O3, NiO, Ga2O3, WO3, ...
- □ **Nitrides:** AIN, TaNx, NbN, TiN, MoN, ZrN, HfN, GaN, WxN, InN, SiNx, ...
- **Carbides:** TiC, NbC, TaC, ...
- □ **Metals:** Pt, Ru, Ir, Pd, Cu, Fe, Co, Ni, W, ...
- □ **Sulfides:** ZnS, SrS, CaS, PbS, ...
- □ **Fluorides:** CaF2, SrF2, ZnF2, ...
- **Biomaterials:** TiO2, Ca10(PO4)6(OH)2 (hydroxyapatite)
- **Polymers/** Polyimides (PMDA-ODA, PMDA-DAH),
 Organic : 3-aminopropyltrimethoxysilane, ...
- **Doping:** ZnO:Al, ZnS:Mn, SrS:Ce, Al2O3:Er, YSZ, ...
- **Nanolaminates:** HfO2/Ta2O5, TiO2/Ta2O5, TiO2/Al2O3, ZnS/Al2O3, ...
- □ Mixed structures: TiAIN, TaAIN, ATO (AITiO), TiCrOx, SiON, LaAIO, STO, ...
- □ Substrate temperature between 25 °C and 500 °C.
- Metal precursor compounds include: halides, organometals, alkoxides, metallocenes, beta diketonates, N-coordinated precursors (amides, amidinates), ...



ALD benefits driven by surface reactions

Saturation and surface control

- Excellent step coverage (trenches, 3D)
- High conformality (thickness, composition)
- Pinhole free structures

Chemisorption

- Primer layers
- Surface modifications

Sequential

- Multi-layers in one process
- Nanolaminates
- Even gradual composition changes in nanoscale





6.2 µm



- Extreme surface conformality The best technology to deposit conformal films with superior uniformity
- Pinhole free films ALD is naturally pinhole free; excellent for passivation, barriers and insulators
- **Repeatability, precision –** without in-situ feedback and control
- □ **Scalability** straightforward to scale-up
- Thin, dense, smooth films <2nm Films formed one atomic layer at a time
- Artificial materials Digital control of ALD provides a way to create artificial materials; a critical benefit in many innovative R&D applications







Artificial Materials by ALD





Artificial Materials by ALD for 3D substrates





Film Thickness Uniformity





ALD Process scalability

If something works in small scale it should work also on industrial scale ???

- performance, integration
- deposition speed
- price

Reaction	chamber
	Cubatrata
	Substrate
Gas in	Gas out





Renewable energy - Photovoltaics





Markets and Applications

Medical industry

Biocompatible thin film coatings







Beneq © 2009



Markets and Applications

Industrial thin film coatings





Barrier applications





www.oled-display.net



Superior Barrier Layer Against Moisture

Ca-test, WVTR $(g/day \cdot m^2)$

Substrate	Process temperature	Condition 80 [°] C/80%			
Са	120 °C	8x10 ⁻⁵ *			

* Corresponds < 10⁻⁶ g/m² day @ RT test performed at TU Braunschweig









Rear Surface Passivation of c-Si Solar Cells

Back surface passivation of thin c-Si cell wafers improves efficiency, through increased effective lifetime of charge carriers





ALD Zn(O,S) buffer layer gives 1%-unit higher efficiency compared to conventional CdS





ALD Zn(O,S) buffer layer for CIGS solar cells

- Improved transmission vs. CdS
- Highly conformal
- Enhanced blocking of pin-holes in the CIGS layer

\rightarrow 1%-unit higher efficiency



Beneq TFS 1200 in-line production ALD system



ALD Zn(O,S) buffer layer for CIGS solar cells - Highly conformal and excellent step coverage



TEM from Uppsala University

ြံ့ BENEQ Buffer Layer for CIGS Solar Cells

Beneq TFS 1200 In-line ALD module

- Substrate 600x1200mm²
- Batch size 2 substrates
- Batch time 5 min
- Thru-put 24pcs/h





For substrates up to 1200x1200mm²

The largest substrate ever coated with ALD!



Beneq 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 600 For PV and display industry
- TFS 1200 In-line ALD equipment for PV
- P400A, P800 Batch ALD equipment for manufacturing

Application examples:

- nOPTO Optical coatings
- nERGY Photovoltaic applications
- nSILVER Anti-tarnishing coatings on silver
- nCLEAR Passivation and hermetic barrier coatings
- nTRIBO Tribological coatings for precision parts
- nPRIMER Primering applications
- Glass strengthening





Industrial scale up









The Myth: The Answer:

ALD is slow and only for ultra-thin films Growth on surface => scale up by expanding surface ALD is a slow in nm/s, but fast in m²/s.







Turning Innovations into Success



Application specific coating and material <u>development</u> services

<u>Verification</u> and pilot production services

Coating equipment

BENED ALD Tool for Research and Development

Thin Film System – TFS 200



Advanced tool for advanced ALD research



Thank You !

Mr. Mikko Saikkonen e-mail:mikko.saikkonen@beneq.com