Atomic Layer Deposition

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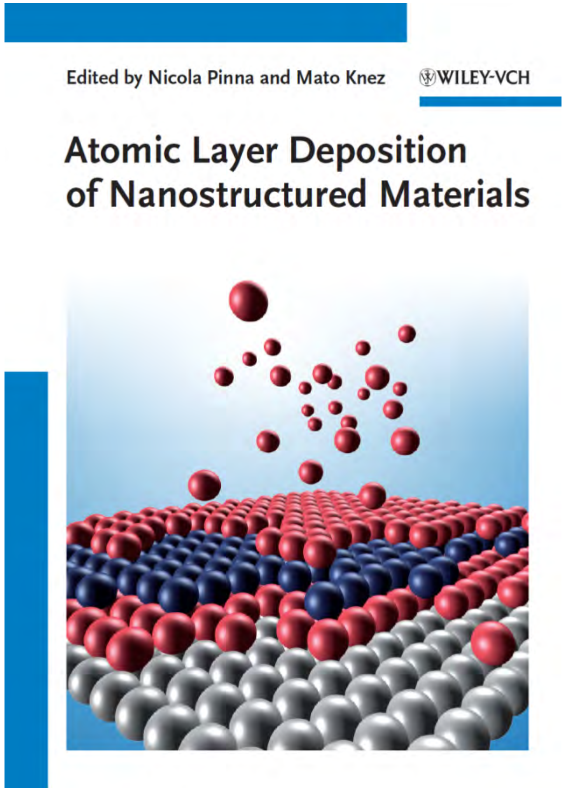
Outline of the Presentation

1. Literature
2. Introduction to Atomic Layer Deposition
3. Chemistry in ALD
4. ALD Reactors
5. Nanostructures
6. Applications



Edited by Nicola Pinna and Mato Knez

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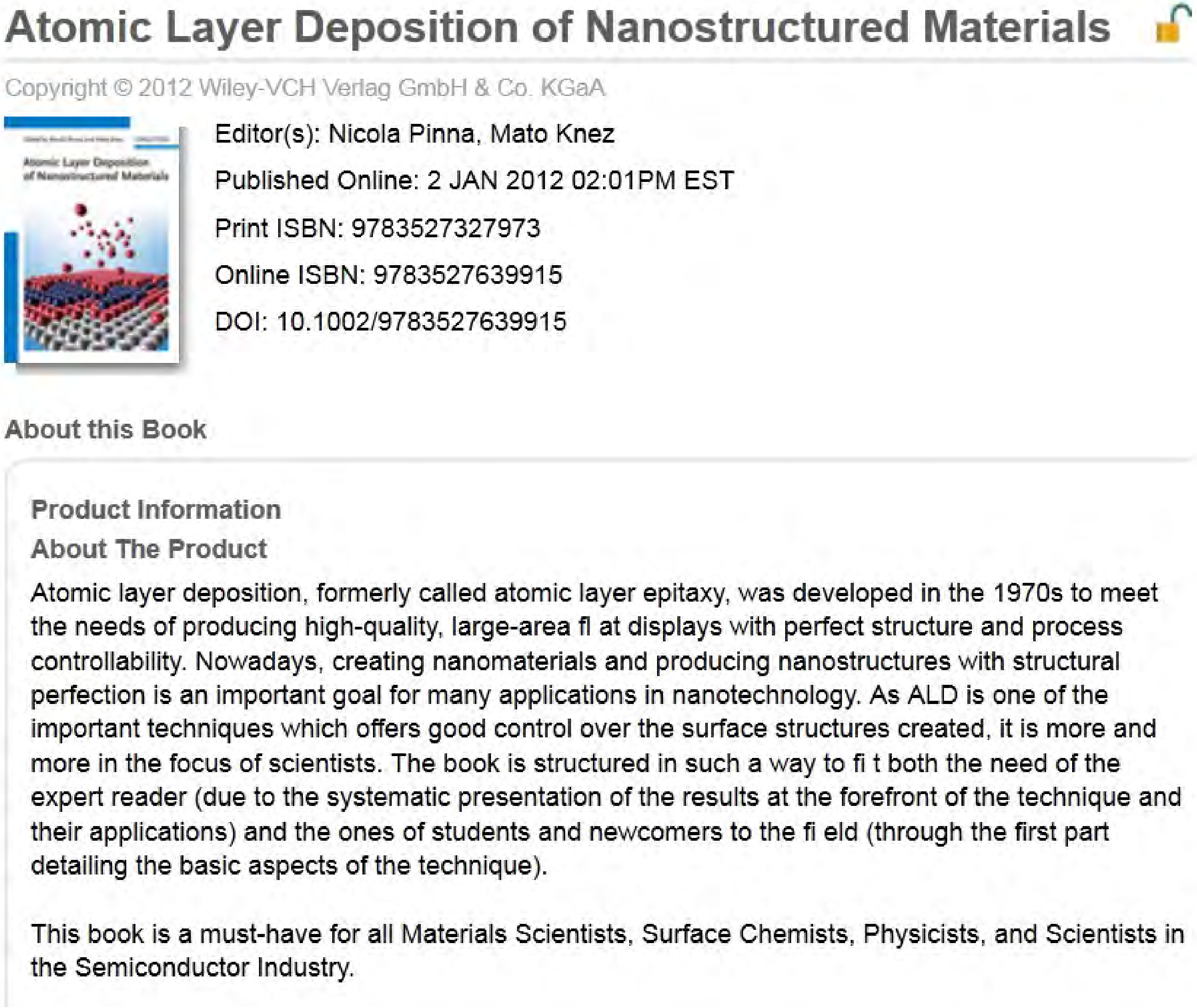
Atomic Layer Deposition
of Nanostructured Materials



Atomic Layer Deposition of Nanostructured Materials

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About this Book

Product Information

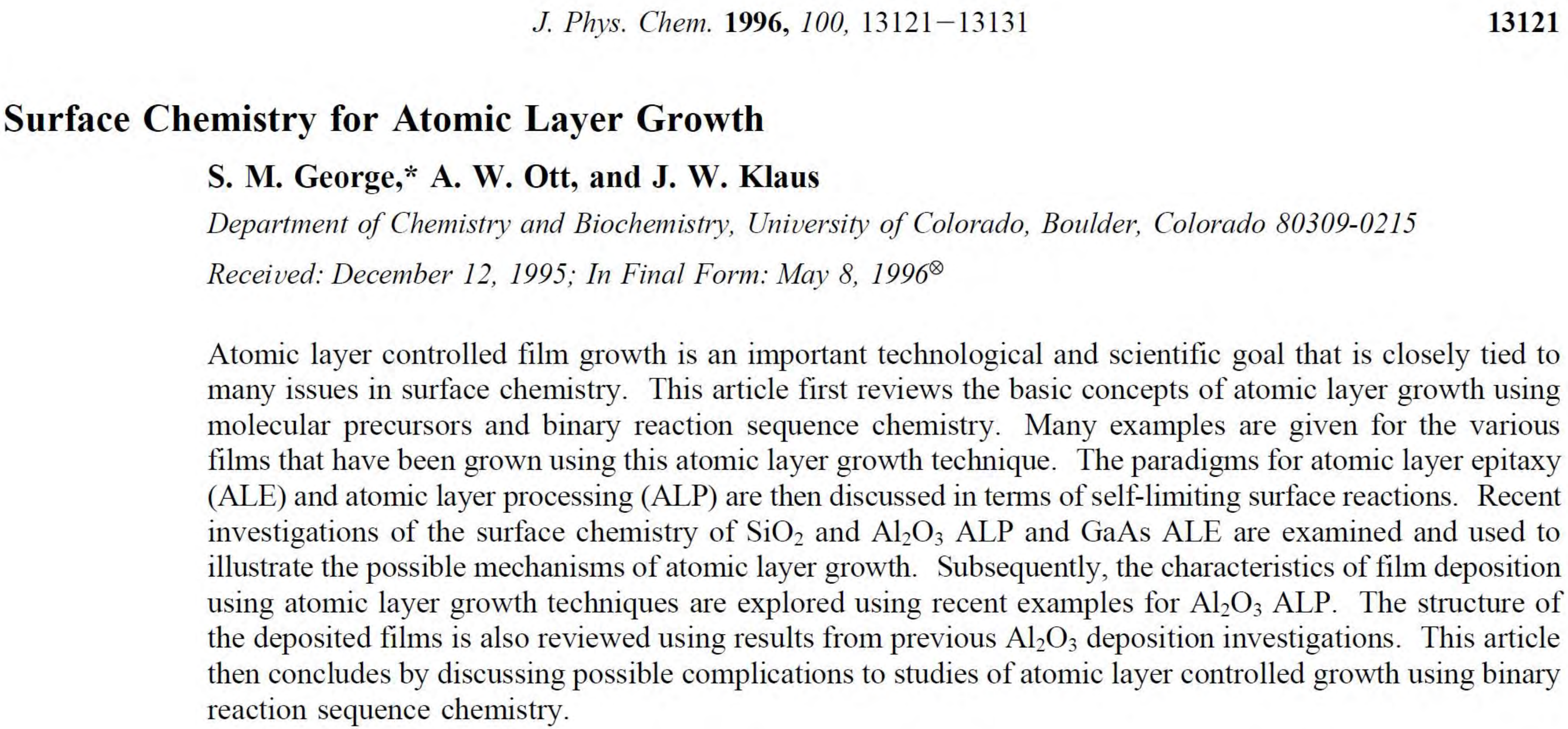
About The Product

Atomic layer deposition, formerly called atomic layer epitaxy, was developed in the 1970s to meet the needs of producing high-quality, large-area flat displays with perfect structure and process controllability. Nowadays, creating nanomaterials and producing nanostructures with structural perfection is an important goal for many applications in nanotechnology. As ALD is one of the important techniques which offers good control over the surface structures created, it is more and more in the focus of scientists. The book is structured in such a way to fit both the need of the expert reader (due to the systematic presentation of the results at the forefront of the technique and their applications) and the ones of students and newcomers to the field (through the first part detailing the basic aspects of the technique).

This book is a must-have for all Materials Scientists, Surface Chemists, Physicists, and Scientists in the Semiconductor Industry.

Part One: Introduction to ALD

Part Two: Nanostructures by ALD



J. Phys. Chem. **1996,** *100,* 13121−13131 **13121**

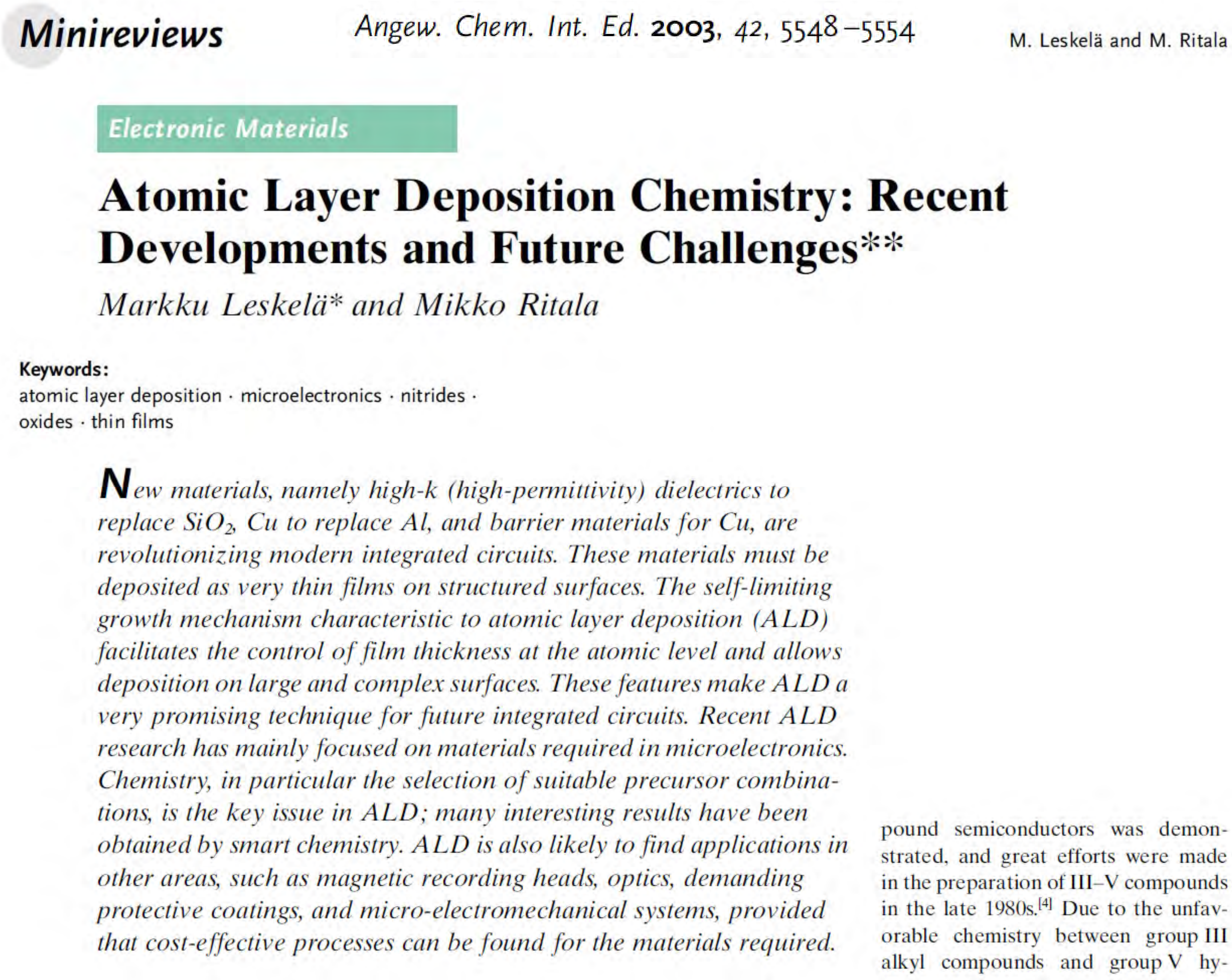
Surface Chemistry for Atomic Layer Growth

S. M. George,* A. W. Ott, and J. W. Klaus

Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215

Received: December 12, 1995; In Final Form: May 8, 1996⊗

Atomic layer controlled film growth is an important technological and scientific goal that is closely tied to many issues in surface chemistry. This article first reviews the basic concepts of atomic layer growth using molecular precursors and binary reaction sequence chemistry. Many examples are given for the various films that have been grown using this atomic layer growth technique. The paradigms for atomic layer epitaxy (ALE) and atomic layer processing (ALP) are then discussed in terms of self-limiting surface reactions. Recent investigations of the surface chemistry of SiO_2 and Al_2O_3 ALP and GaAs ALE are examined and used to illustrate the possible mechanisms of atomic layer growth. Subsequently, the characteristics of film deposition using atomic layer growth techniques are explored using recent examples for Al_2O_3 ALP. The structure of the deposited films is also reviewed using results from previous Al_2O_3 deposition investigations. This article then concludes by discussing possible complications to studies of atomic layer controlled growth using binary reaction sequence chemistry.



Minireviews Angew. Chem. Int. Ed. **2003**, 42, 5548–5554 M. Leskelä and M. Ritala

Electronic Materials

Atomic Layer Deposition Chemistry: Recent Developments and Future Challenges**

Markku Leskelä and Mikko Ritala*

Keywords:
atomic layer deposition · microelectronics · nitrides · oxides · thin films

New materials, namely high-k (high-permittivity) dielectrics to replace SiO_2, Cu to replace Al, and barrier materials for Cu, are revolutionizing modern integrated circuits. These materials must be deposited as very thin films on structured surfaces. The self-limiting growth mechanism characteristic to atomic layer deposition (ALD) facilitates the control of film thickness at the atomic level and allows deposition on large and complex surfaces. These features make ALD a very promising technique for future integrated circuits. Recent ALD research has mainly focused on materials required in microelectronics. Chemistry, in particular the selection of suitable precursor combinations, is the key issue in ALD; many interesting results have been obtained by smart chemistry. ALD is also likely to find applications in other areas, such as magnetic recording heads, optics, demanding protective coatings, and micro-electromechanical systems, provided that cost-effective processes can be found for the materials required.

pound semiconductors was demonstrated, and great efforts were made in the preparation of III–V compounds in the late 1980s.[4] Due to the unfavorable chemistry between group III alkyl compounds and group V hy-

JOURNAL OF APPLIED PHYSICS **97**, 121301 (2005)

APPLIED PHYSICS REVIEWS

Surface chemistry of atomic layer deposition: A case
for the trimethylaluminum/water process

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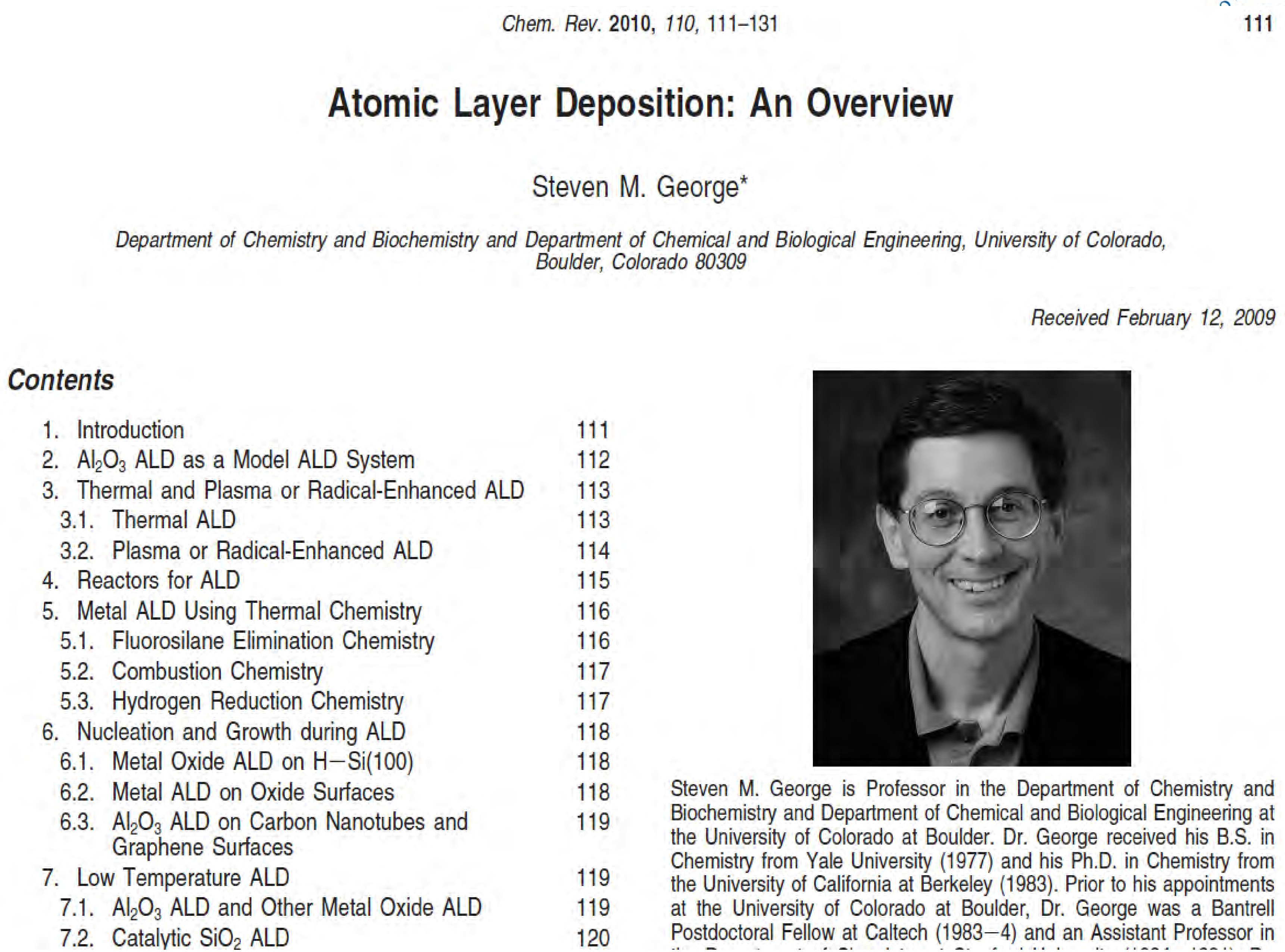
Atomic layer deposition (ALD), a chemical vapor deposition technique b
self-terminating gas–solid reactions, has for about four decades been applied
conformal inorganic material layers with thickness down to the nanometer
numerous successful applications of material growth by ALD, many physicoche
control ALD growth are not yet sufficiently understood. To increase und
processes, overviews are needed not only of the existing ALD processes and th
also of the knowledge of the surface chemistry of specific ALD processes. Thi
the overviews on specific ALD processes by reviewing the experimental infor
the surface chemistry of the trimethylaluminum/water process. This process is
a rather ideal ALD process, and plenty of information is available on its surf
in-depth summary of the surface chemistry of one representative ALD process
a view on the current status of understanding the surface chemistry of ALD, in
starts by describing the basic characteristics of ALD, discussing the history of
question who made the first ALD experiments—and giving an overview of the
processes investigated to date. Second, the basic concepts related to the surface
are described from a generic viewpoint applicable to all ALD processes b
reactants. This description includes physicochemical requirements for self-ter
reaction kinetics, typical chemisorption mechanisms, factors causing saturation,
of less than a monolayer per cycle, effect of the temperature and number of cycl
cycle (GPC), and the growth mode. A comparison is made of three models avai
the sterically allowed value of GPC in ALD. Third, the experimental informa
chemistry in the trimethylaluminum/water ALD process are reviewed using the
in the second part of this review. The results are reviewed critically, with an
information obtained in different types of investigations, such as growth e
substrates and reaction chemistry investigation on high-surface-area materials. A
chemistry of the trimethylaluminum/water ALD process is rather well und
investigations of the reaction kinetics and the growth mode on different substra
The last part of the review is devoted to discussing issues which may hampe
investigations of ALD, such as problematic historical assumptions, nonstanda
the effect of experimental conditions on the surface chemistry of ALD. I hope
help the newcomer get acquainted with the exciting and challenging field of s
ALD and can serve as a useful guide for the specialist towards the fifth decad
© 2005 American Institute of Physics. [DOI: 10.1063/1.1940727]

TABLE III. Overview of ALD processes based on two reactants (Source: ISI Web of Science, status in February 2005). Description of the ligands in Fig. 4.

Z	Material	Reactant *A*[a]	Reactant *B*	Refs.
5 Boron				
	B_2O_3	BBr_3	H_2O	85
	BN	BCl_3	NH_3	158
		BBr_3	NH_3	159
	$B_xP_yO_z$	$B(OMe)_3$	$POCl_3$	88 and 89
6 Carbon				
	C[b]	CF_x	H[c]	160
		CCl_3	H[c]	161
12 Magnesium				
	MgO	$MgCp_2$	H_2O	162–166
		$Mg(thd)_2$	H_2O_2	167
		$Mg(thd)_2$	O_3	168
	MgTe	Mg	Te	169 and 170
13 Aluminum				
	Al_2O_3	$AlCl_3$	H_2O	76, 77, 83, 90, 91, 91, and 171–184
		$AlCl_3$	O_2	185 and 186
		$AlCl_3$	*ROH*[d]	173, 181, and 187
		$AlCl_3$	$Al(OEt)_3$	188
		$AlCl_3$	$Al(O^iPr)_3$	188 and 189
		$AlBr_3$	H_2O	92
		$AlMe_3$	H_2O	166, 179, and 190–262
		$AlMe_3$	H_2O_2	263–269
		$AlMe_3$	O_3	236, 244, 245, and 270–273
		$AlMe_3$	O_2[e]	274–276
		$AlMe_3$	N_2O	266
		$AlMe_3$	NO_2	194
		$AlMe_3$	N_2O_4	151
		$AlMe_3$	^iPrOH	277
		$AlMe_3$	$Al(O^iPr)_3$	188
		$AlMe_2Cl$	H_2O	278
		$AlMe_2O^iPr$	H_2O	279 and 280
		$AlEt_3$	H_2O	163
		$Al(OEt)_3$	H_2O	173
		$Al(OEt)_3$	O_2	173
		$Al(O^nPr)_3$	H_2O	173 and 181
		$Al(O^nPr)_3$	O_2	281
	AlN	$AlCl_3$	NH_3	282 and 283
		$AlCl_3$	NH_3+H_2[e]	284 and 285
		$AlMe_3$	NH_3	209, 216, 283, and 286–292
		$AlEt_3$	NH_3	293 and 294
		$Me_3N:AlH_3$	NH_3	295
		$Me_2EtN:AlH_3$	NH_3	296–298
	AlP	$AlMe_2H$	PH_3	299–301
		$Me_2EtN:AlH_3$	PH_3	302
	AlAs	$AlCl_3$	AsH_3	303 and 304
		$AlMe_3$	AsH_3	305–315
		$AlMe_2H$	AsH_3	316–320
		$AlEt_3$	AsH_3	309 and 311
		Al^iBu_3	AsH_3	321
		$Me_3N:AlH_3$	AsH_3	322
		$Me_3N:AlH_3$	$As(NMe_2)_3$	323 and 324
		$Me_2EtN:AlH_3$	AsH_3	320 and 325–330
	Al	$AlMe_3$	H_2[e]	331 and 332
	$Al_xSi_yO_z$	$AlCl_3$	$Si(OEt)_4$	94
	Al_2O_3/SiO_2[f]	$AlMe_3$	$(^tBuO)_3SiOH$	157
	$Al_xTi_yO_z$	$AlCl_3$	$Ti(OEt)_4$	188
		$AlCl_3$	$Ti(O^iPr)_4$	188
		$AlMe_3$	$Ti(O^iPr)_4$	188



Chem. Rev. **2010**, *110*, 111–131

Atomic Layer Deposition: An Overview

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Contents

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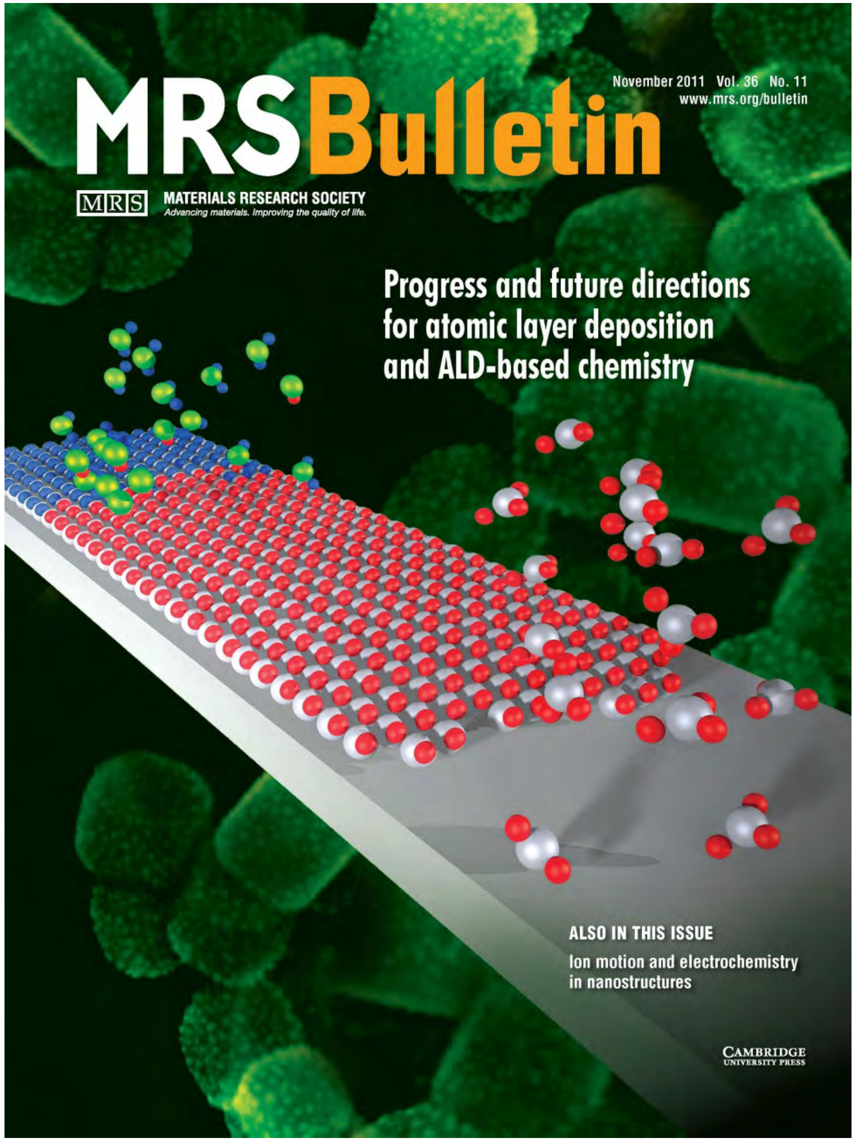
ADVANCED MATERIALS

Adv. Mater. **2007**, *19*, 3425–3438

Synthesis and Surface Engineering of Complex Nanostructures by Atomic Layer Deposition**

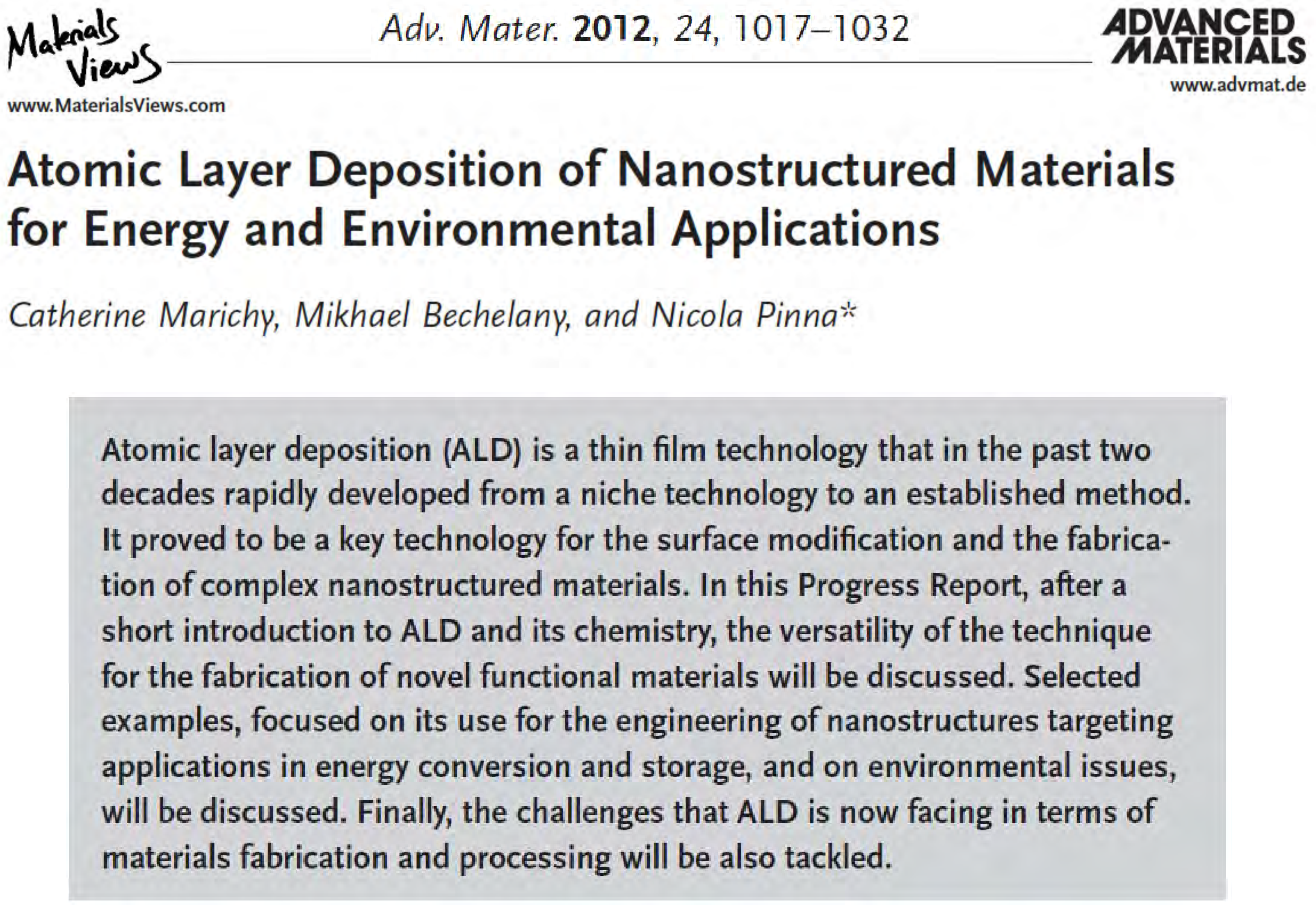
By *Mato Knez*,* *Kornelius Nielsch*, and *Lauri Niinistö*

Atomic layer deposition (ALD) has recently become the method of choice for the semiconductor industry to conformally process extremely thin insulating layers (high-k oxides) onto large-area silicon substrates. ALD is also a key technology for the surface modification of complex nanostructured materials. After briefly introducing ALD, this Review will focus on the various aspects of nanomaterials and their processing by ALD, including nanopores, nanowires and -tubes, nanopatterning and nanolaminates as well as low-temperature ALD for organic nanostructures and biomaterials. Finally, selected examples will be given of device applications, illustrating recent innovative approaches of how ALD can be used in nanotechnology.



Progress and future directions for atomic layer deposition and ALD-based chemistry. This issue of *MRS Bulletin* details current progress in atomic layer deposition, including the extension of ALD to new regions of the periodic table, and molecular layer deposition and vapor in filtration for synthesis of organic based thin films. The cover image shows a diagram of an ALD reaction scheme–a snapshot of the reactants and products as they would be flowing from left to right. This is a general, stylized ALD reaction scheme to visualize surface ligand exchange. The background is a scanning electron microscopy image of 2 nm ALD-deposited Pt nanoparticles uniformly dispersed on strontium titanate nanocubes.

MRS Bulletin / Volume 36 / Issue 11 / November 2011, pp 899-906



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Adv. Mater. **2012**, *24*, 1017–1032

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Atomic Layer Deposition of Nanostructured Materials for Energy and Environmental Applications

*Catherine Marichy, Mikhael Bechelany, and Nicola Pinna**

Atomic layer deposition (ALD) is a thin film technology that in the past two decades rapidly developed from a niche technology to an established method. It proved to be a key technology for the surface modification and the fabrication of complex nanostructured materials. In this Progress Report, after a short introduction to ALD and its chemistry, the versatility of the technique for the fabrication of novel functional materials will be discussed. Selected examples, focused on its use for the engineering of nanostructures targeting applications in energy conversion and storage, and on environmental issues, will be discussed. Finally, the challenges that ALD is now facing in terms of materials fabrication and processing will be also tackled.

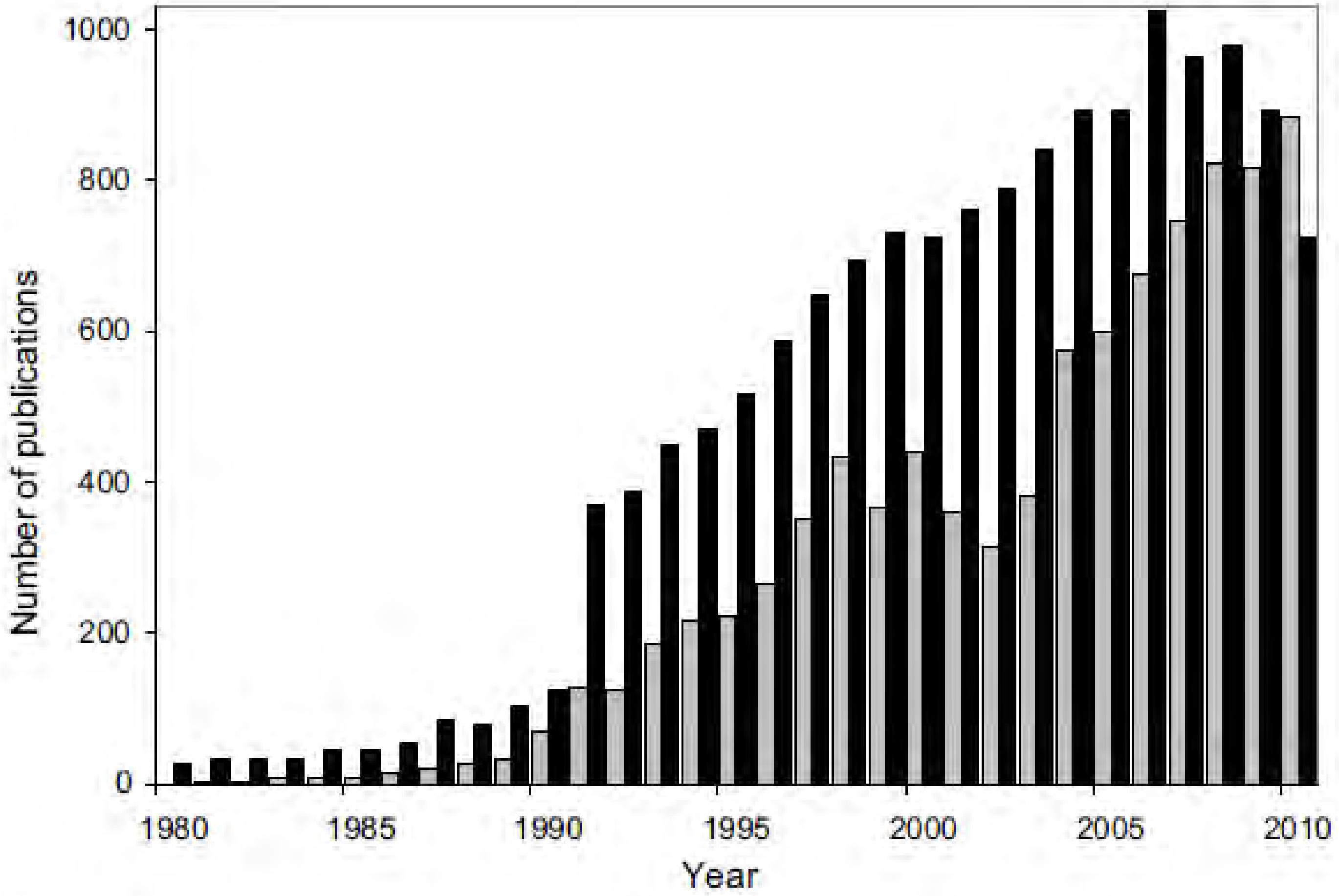
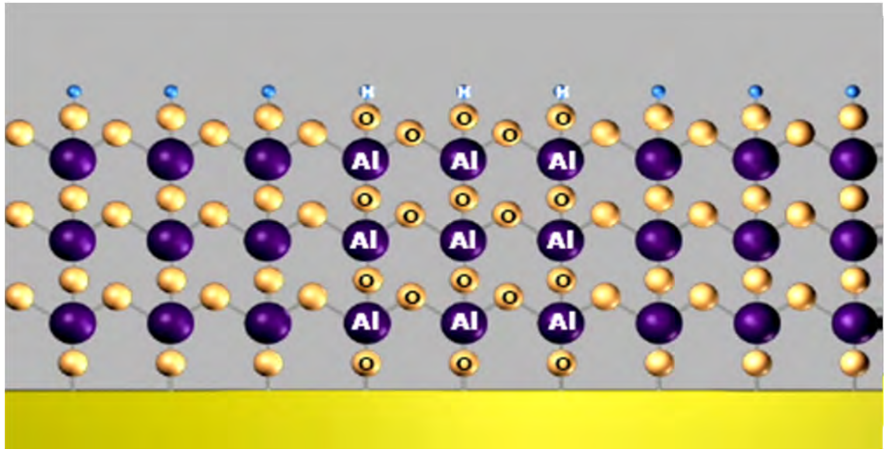


Figure P.1 Number of articles per year published on ALD (gray bars) and CVD divided by five (black bars). *Source:* Web of Science accessed on December 20, 2010.

Atomic Layer Deposition of Nanostructured Materials, First Edition. Edited by Nicola Pinna and Mato Knez.

Atomic Layer Deposition

- ALD is a method for depositing thin films onto various substrates with **atomic scale precision**.
- The principle is **similar to chemical vapor deposition** (CVD), except that the ALD **reactions are separated** into two half-reactions by keeping the precursor materials separate during the reaction.
- ALD film growth is **self-limited** and based on **surface reactions**. Therefore, film thickness control can be as fine as one monolayer.



ALD can be defined as a film deposition technique that is based on the sequential use of self-terminating gas–solid reactions.[68–70] The growth of material layers by ALD consists of repeating the following characteristic four steps:

(1) A self-terminating reaction of the first reactant (Reactant *A*).
(2) A purge or evacuation to remove the nonreacted reactants and the gaseous reaction by-products.
(3) A self-terminating reaction of the second reactant (Reactant *B*)—or another treatment to activate the surface again for the reaction of the first reactant.[71]
(4) A purge or evacuation.

Steps 1–4 constitute a *reaction cycle*. Steps 1 and 3 are sometimes referred to as *half reactions* of an ALD reaction cycle.[40,72]

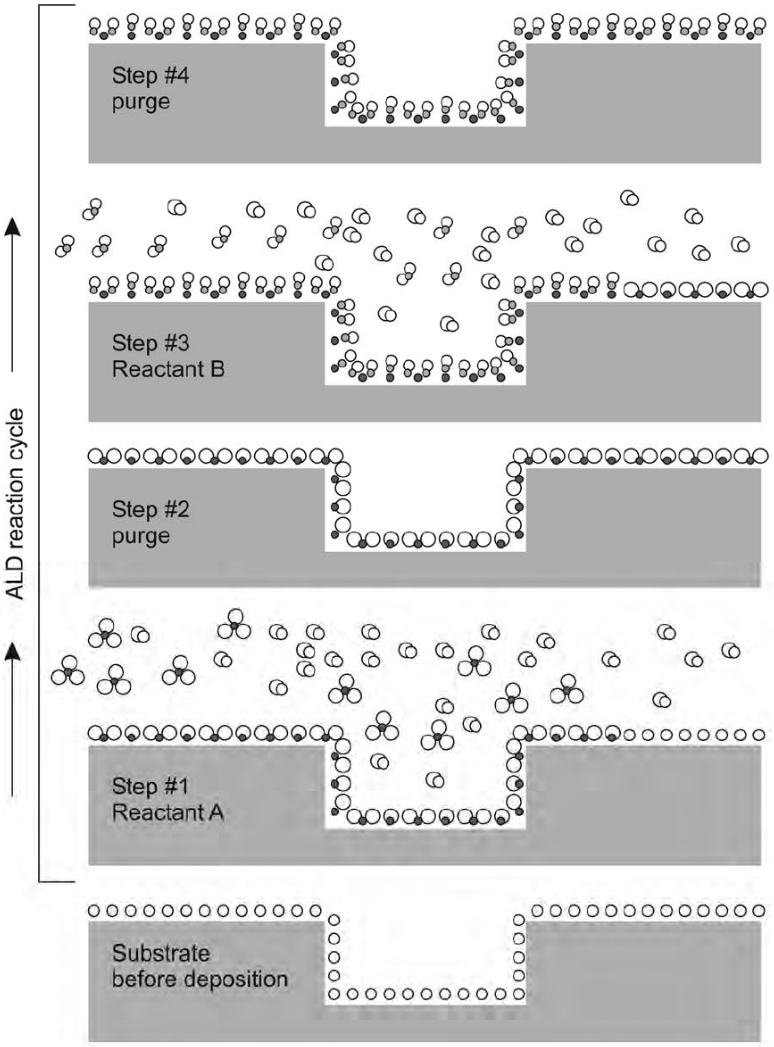


FIG. 2. Schematic illustration of one ALD reaction cycle.

Riikka L. Puurunen, *J. Appl. Phys.*, **2005**, 97, 121301

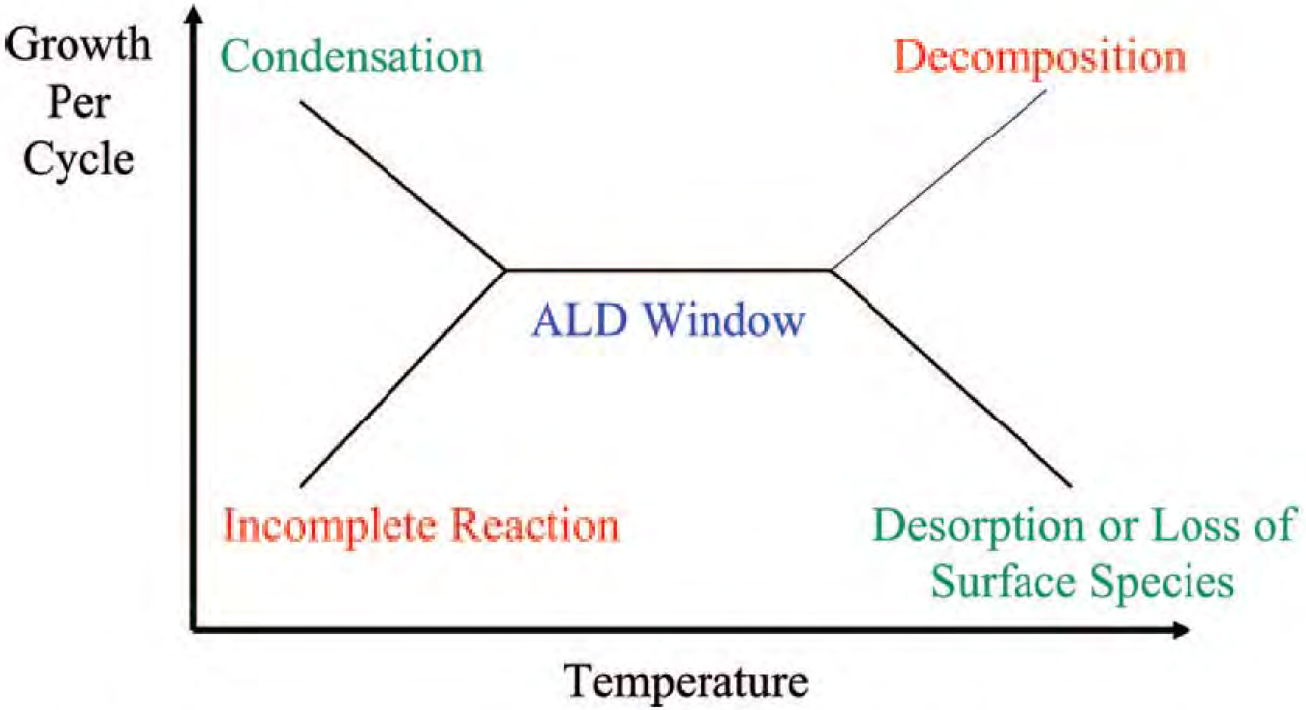
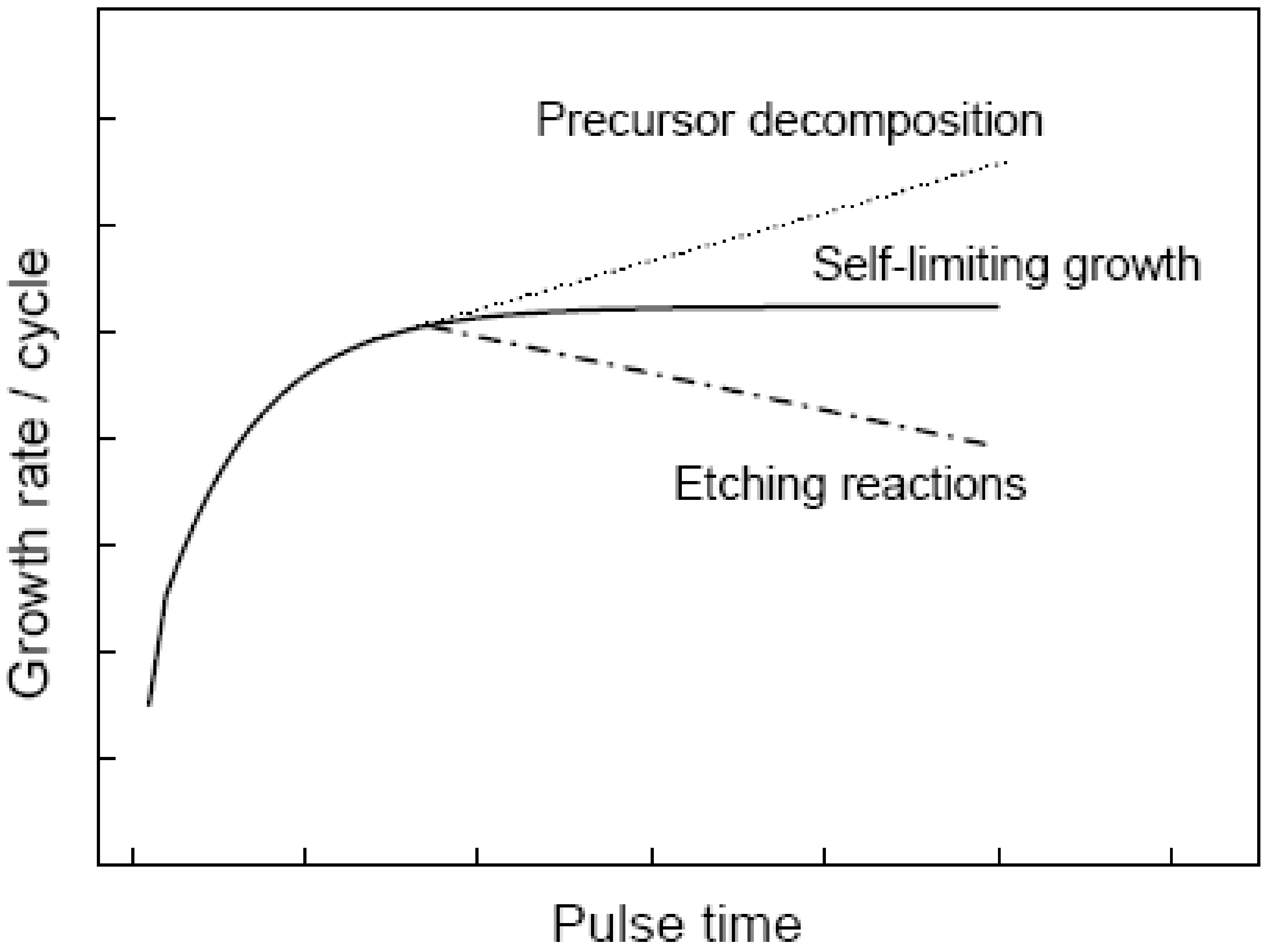


Figure 25. Schematic of possible behavior for the ALD growth per cycle versus temperature showing the "ALD" window. (Adapted from ref 12.)


Precursor decomposition
Self-limiting growth
Etching reactions
Growth rate / cycle
Pulse time

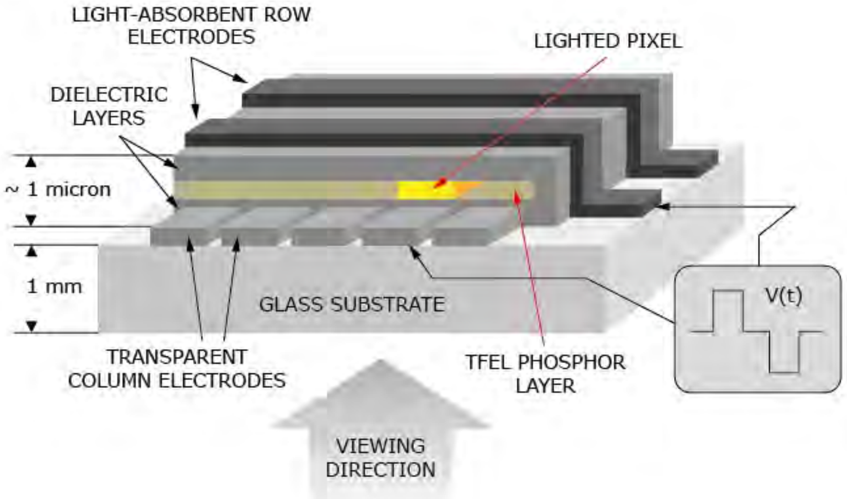
Short History

1970s - The ALD technology was developed in Finland and patented.
Technology for thin films electroluminescent (TFEL) flat panel display.
Suntola, T. and Antson, J., Method for producing compound thin films, US Patent 4 058 430 (1977).
At that time the technique was called Atomic Layer Epitaxy (ALE)

TFEL displays commercialized in 1980 were based on ALD $Al_2O_3/ZnS:Mn/Al_2O_3$ structures

Time Zeit	Flight Flug	Destination/via Richtung /über	Counter Schalter	Remarks Bemerkungen
0935	FR 8559	Dublin		Einstieg
0945	NRD 716	Palma Mallorca	A10/A11	Einstieg
0945	SU 112	Moskau SVO		Einstieg
1000	FV 242	StPetersburg	A12/A13	Abfertigung
1000	DY 1161	Bergen	A16-A18	Abfertigung
1010	EZY4426	Mailand MXP	B23-B27	Abfertigung
1015	4U 8972	Zagreb	D42/D43	Abfertigung
1020	DY 1103	Oslo	A16-A18	Abfertigung
1020	FR 8543	London STN	A06/A07	Einstieg
1025	4U 8086	München	D40/D41	Abfertigung
1035	EZY7820	Madrid	B23-B27	Abfertigung
1040	EI 335	Dublin	A04/A05	Abfertigung
1055	LY 352	Tel Aviv	C30-C34	Abfertigung
1100	AB 5680	Las Palmas	A14/A15	Abfertigung
1100	EZYZ114	London LTN	B23-B27	Abfertigung

Ein Flughafendisplay, dessen elektrolumineszente Beschichtung durch das ALD-Verfahren hergestellt wurde. Das Verfahren wurde für diesen Zweck Ende der siebziger Jahre entwickelt.



Source: http://lumineq.com/en/technology

Source: http://www.weltderphysik.de/gebiete/stoffe/duenne-schichten-und-oberflaechen/atomic-layer-deposition/

Short History

Mid-1980s to the mid-1990s - The ALD research was extremely active on the epitaxial growth of III-V, II-VI, Si and Ge semiconductors

Beginning of the 21th-century- Microelectronic industry drives the development of the ALD due to the continuous scaling of microelectronic devices

1st application: ALD of Al_2O_3 insulating layers in DRAM capacitors due to the need of rather thin and conformal coating of high aspect ratio structures

2007: Intel announces the use of HfO_2-based high-κ gate oxides in CMOS transistors ALD

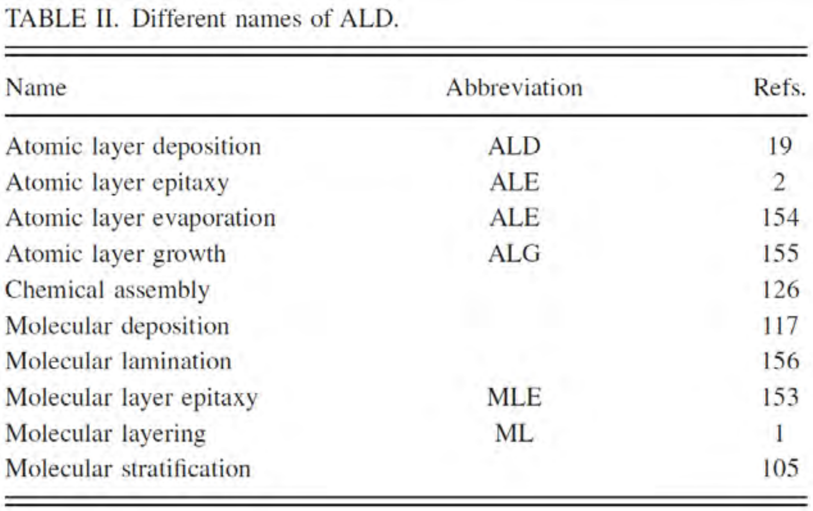
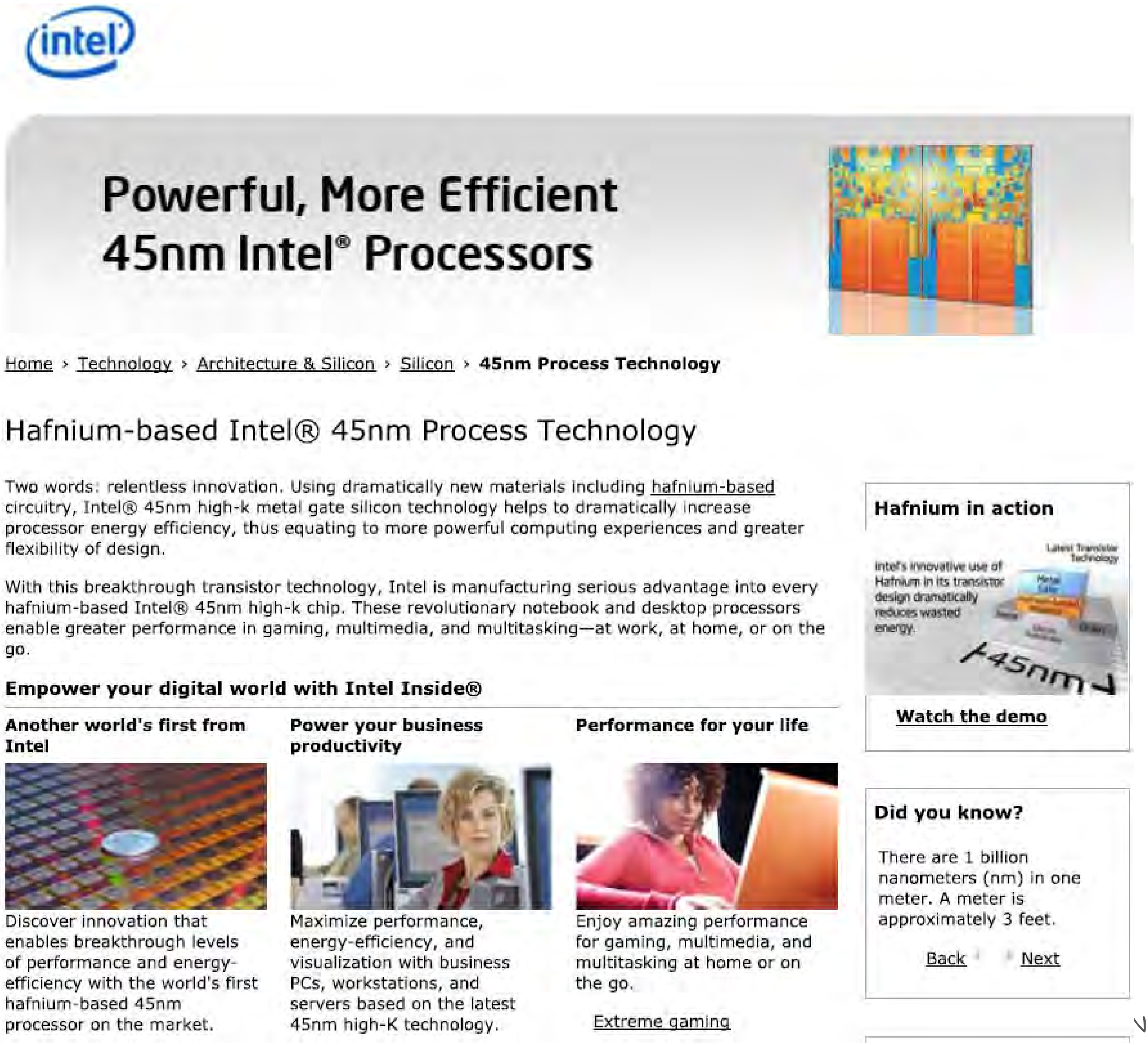


TABLE II. Different names of ALD.

Name	Abbreviation	Refs.
Atomic layer deposition	ALD	19
Atomic layer epitaxy	ALE	2
Atomic layer evaporation	ALE	154
Atomic layer growth	ALG	155
Chemical assembly		126
Molecular deposition		117
Molecular lamination		156
Molecular layer epitaxy	MLE	153
Molecular layering	ML	1
Molecular stratification		105

Intel in 2007 introduced ALD of Hf-based oxide in 45 nm technology



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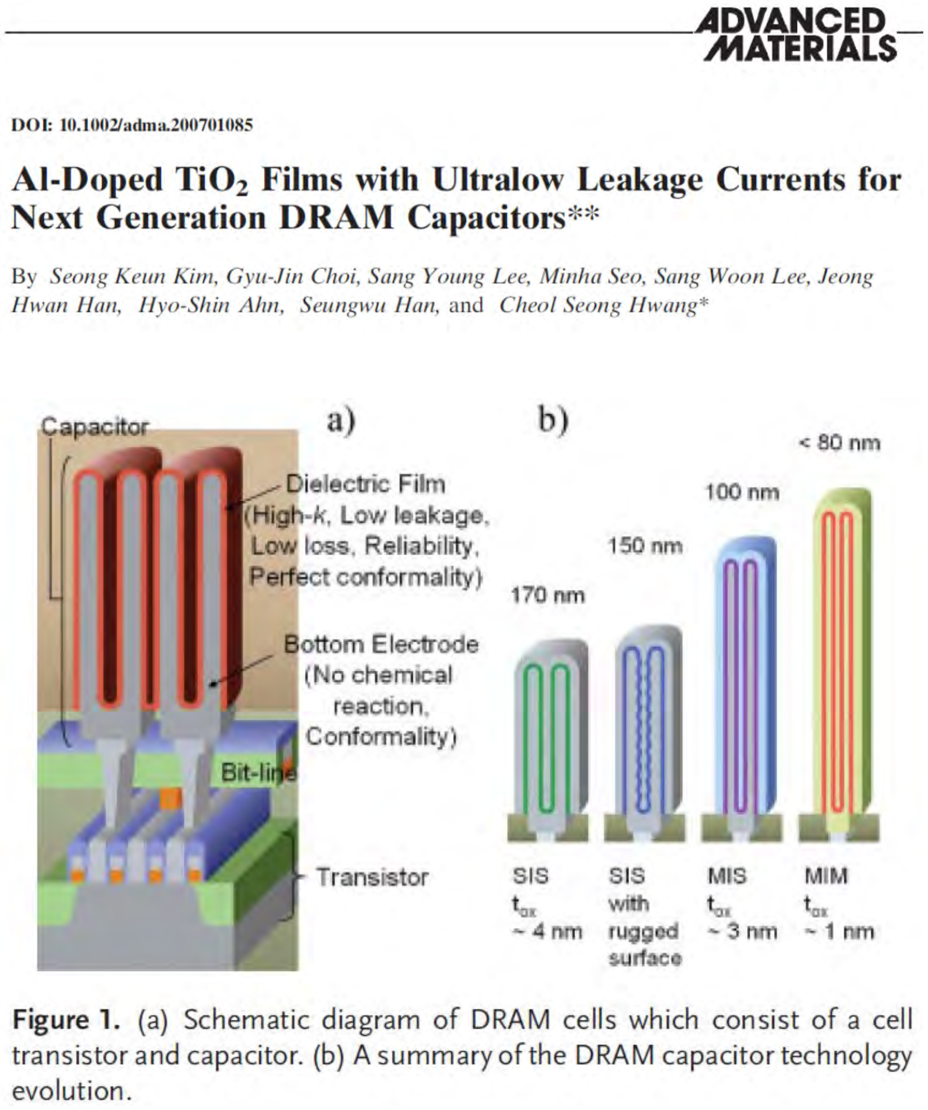
Did you know?

There are 1 billion nanometers (nm) in one meter. A meter is approximately 3 feet.

Back Next


ADVANCED MATERIALS

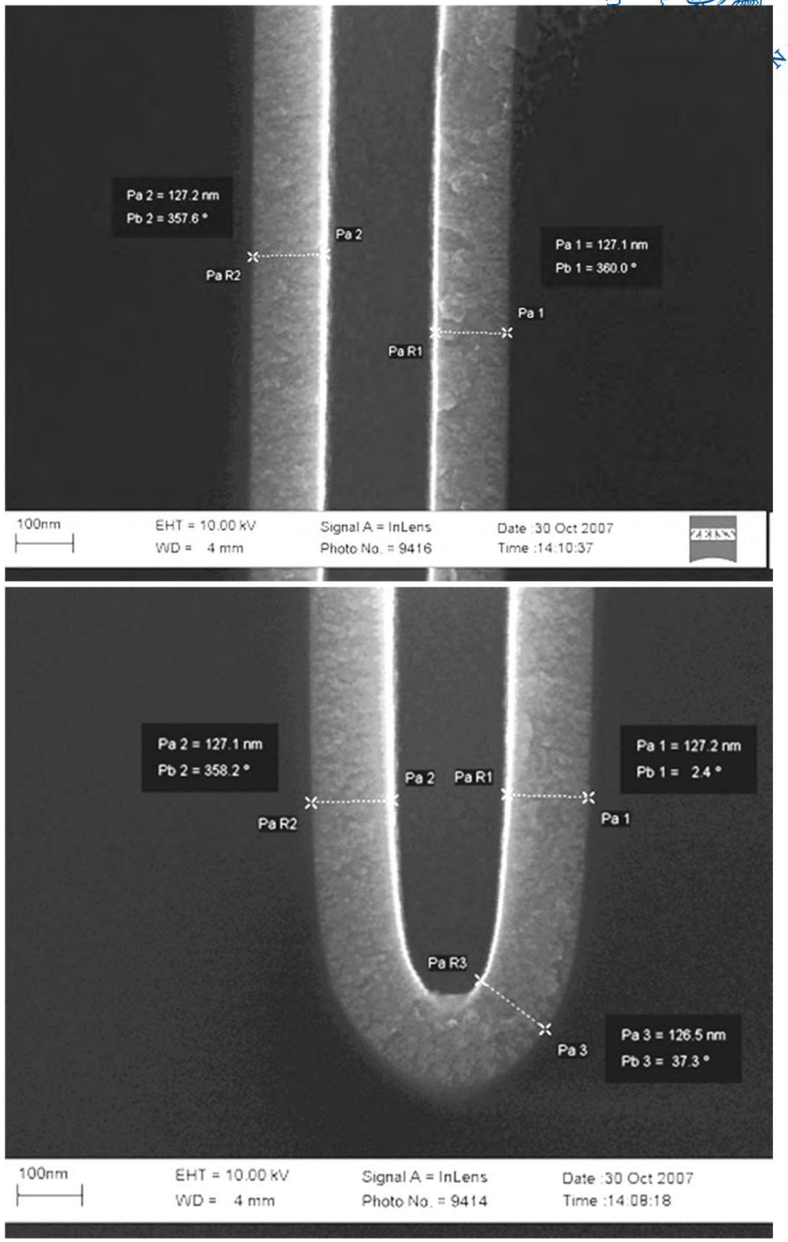
DOI: 10.1002/adma.200701085

Al-Doped TiO_2 Films with Ultralow Leakage Currents for Next Generation DRAM Capacitors**

By *Seong Keun Kim, Gyu-Jin Choi, Sang Young Lee, Minha Seo, Sang Woon Lee, Jeong Hwan Han, Hyo-Shin Ahn, Seungwu Han,* and *Cheol Seong Hwang**

Figure 1. (a) Schematic diagram of DRAM cells which consist of a cell transistor and capacitor. (b) A summary of the DRAM capacitor technology evolution.

Adv. Mater. **2008**, *20*, 1429–1435



http://nano.tkk.fi/en/research_groups/microfabrication/research/microfabrication/

Introduction to the Chemistry Employed in ALD

Requirements for the precursors:

- Reasonably high vapor pressure in order to allow saturation of the chamber volume upon dosing
- Good thermal stability to avoid decomposition prior to the next step
- Must chemisorb onto the substrate to be coated

Oxides:

- Hydrolysis-Condensations
- Oxygen sources (H_2O, H_2O_2, O_3,...)

Nitrides:

- Aminolysis (e.g. NH_3)

Sulfides:

- Sulfur, Hydrogen sulfide

Metals:

- O_2, H_2, etc.

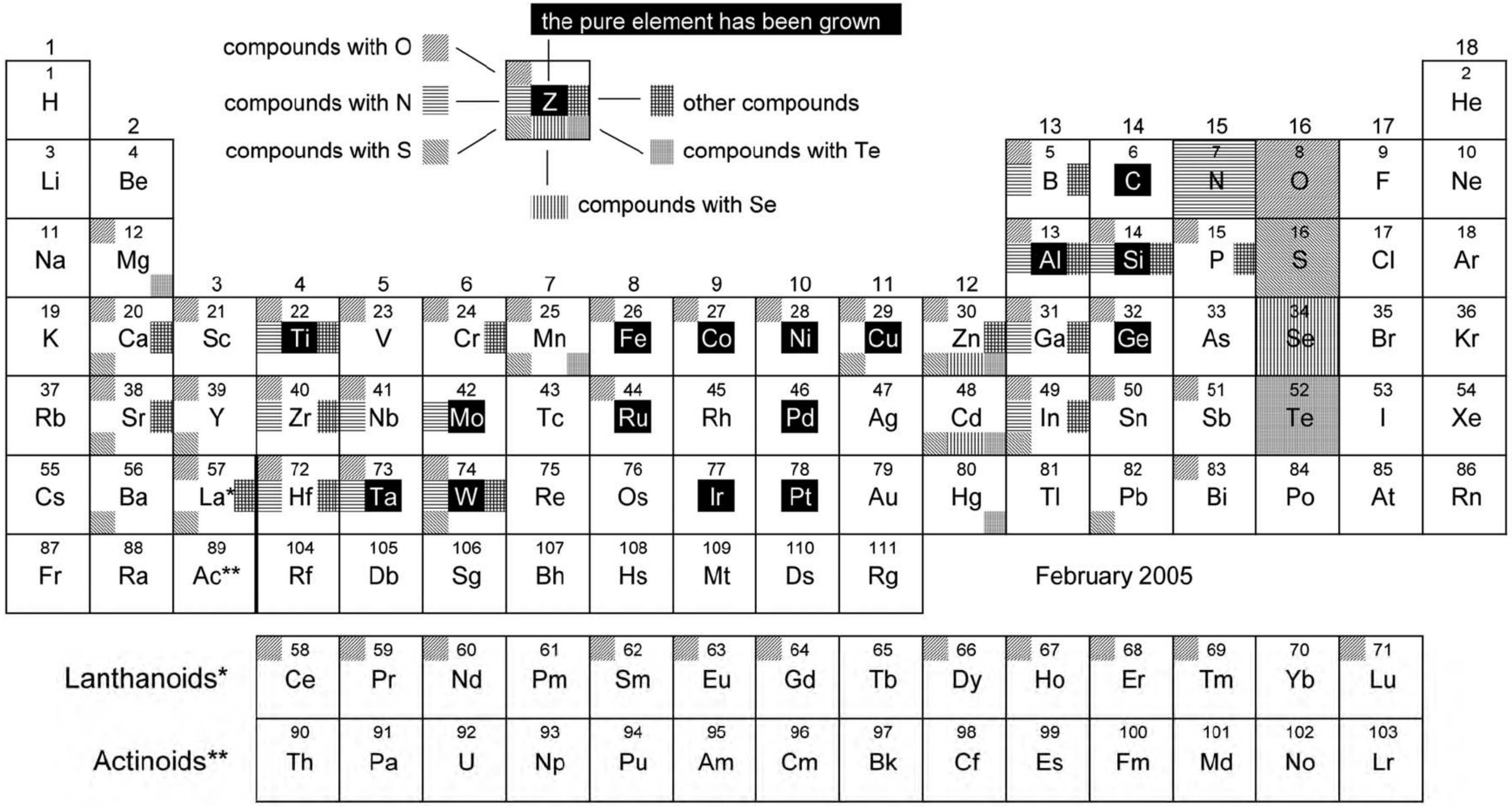
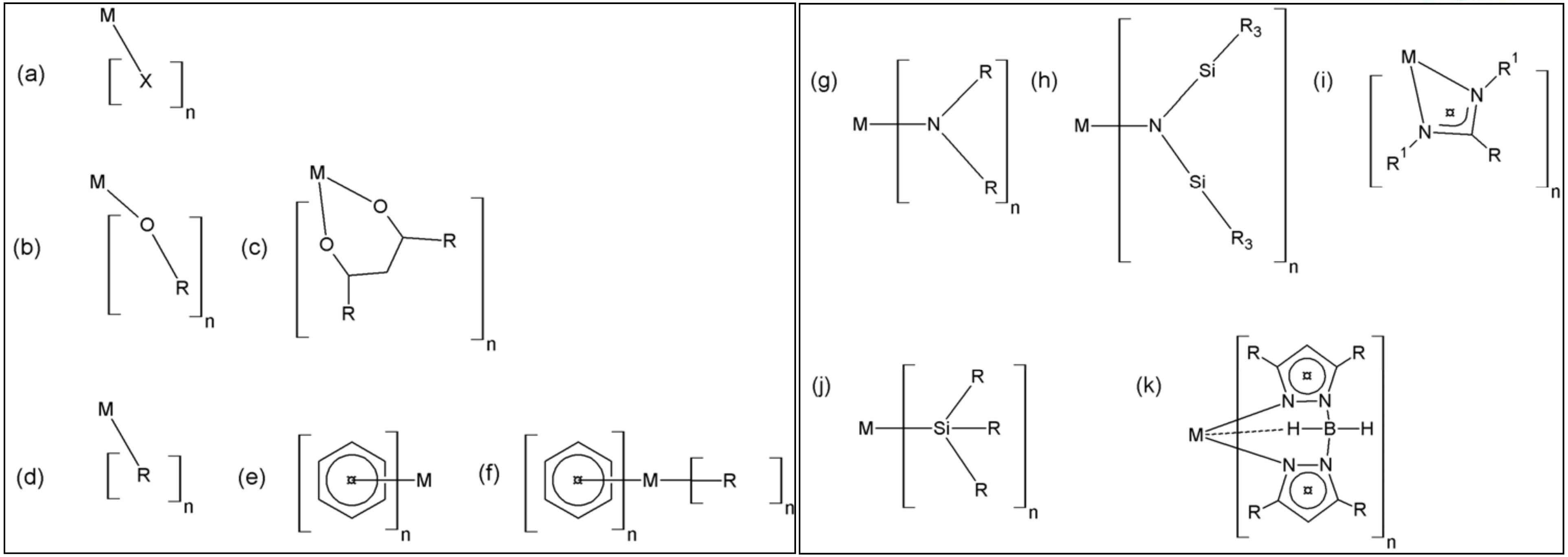


FIG. 3. Overview of the materials grown by ALD. Classification according to Reactant *A*, with details of the investigations in Table III. Growth of pure elements as well as compounds with oxygen, nitrogen, sulphur, selenium, tellurium, and other compounds grouped together are indicated through shadings 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).

J. Appl. Phys. **97**, 121301 (2005)

Metal Precursors



Scheme 3.1 Examples of precursors for ALD depositions. Volatile halides (a), alkoxides (b), and β-diketonates (c) are traditionally used as ALD precursors. Organometallic precursors such as metal alkyls (d) and homo- and heteroleptic cyclopentadienyl-type compounds (e and f) have often favorable properties. Nitrogen-coordinated compounds such as metal amides (g), silylamides (h), amidinates (i), and guanidinates (i, if R = NR_2) have also been successfully applied to ALD. More recently, alkylsilyl compounds (j) and pyrazolyl borate-type ligands (k) have been used for the demanding ALD processes.

M. Putkonen, Chapter 3: Precursors for ALD Processes

Atomic Layer Deposition of Nanostructured Materials, First Edition. Edited by Nicola Pinna and Mato Knez.

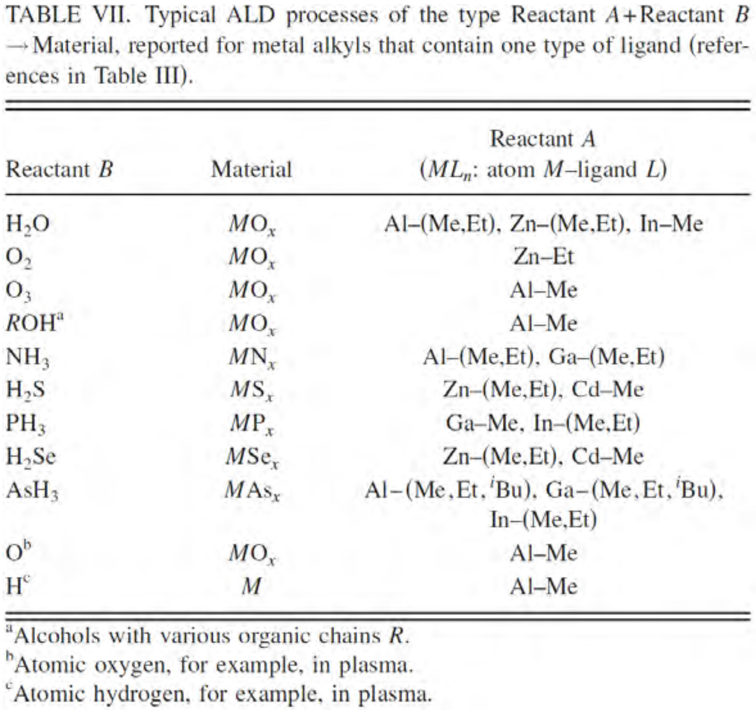


TABLE VII. Typical ALD processes of the type Reactant A+Reactant B → Material, reported for metal alkyls that contain one type of ligand (references in Table III).

Reactant B	Material	Reactant A (ML_n: atom M–ligand L)
H_2O	MO_x	Al–(Me,Et), Zn–(Me,Et), In–Me
O_2	MO_x	Zn–Et
O_3	MO_x	Al–Me
ROH[a]	MO_x	Al–Me
NH_3	MN_x	Al–(Me,Et), Ga–(Me,Et)
H_2S	MS_x	Zn–(Me,Et), Cd–Me
PH_3	MP_x	Ga–Me, In–(Me,Et)
H_2Se	MSe_x	Zn–(Me,Et), Cd–Me
AsH_3	MAs_x	Al–(Me,Et,^{i}Bu), Ga–(Me,Et,^{i}Bu), In–(Me,Et)
O[b]	MO_x	Al–Me
H[c]	M	Al–Me

[a] Alcohols with various organic chains R.

[b] Atomic oxygen, for example, in plasma.

[c] Atomic hydrogen, for example, in plasma.

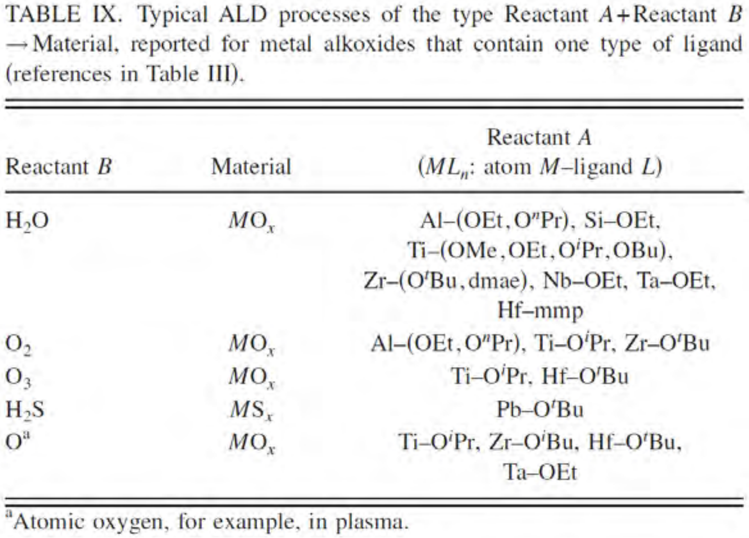


TABLE IX. Typical ALD processes of the type Reactant A+Reactant B → Material, reported for metal alkoxides that contain one type of ligand (references in Table III).

Reactant B	Material	Reactant A (ML_n: atom M–ligand L)
H_2O	MO_x	Al–(OEt,O^{n}Pr), Si–OEt, Ti–(OMe,OEt,O^{i}Pr,OBu), Zr–(O^{t}Bu,dmae), Nb–OEt, Ta–OEt, Hf–mmp
O_2	MO_x	Al–(OEt,O^{n}Pr), Ti–O^{i}Pr, Zr–O^{t}Bu
O_3	MO_x	Ti–O^{i}Pr, Hf–O^{t}Bu
H_2S	MS_x	Pb–O^{t}Bu
O[a]	MO_x	Ti–O^{i}Pr, Zr–O^{t}Bu, Hf–O^{t}Bu, Ta–OEt

[a] Atomic oxygen, for example, in plasma.

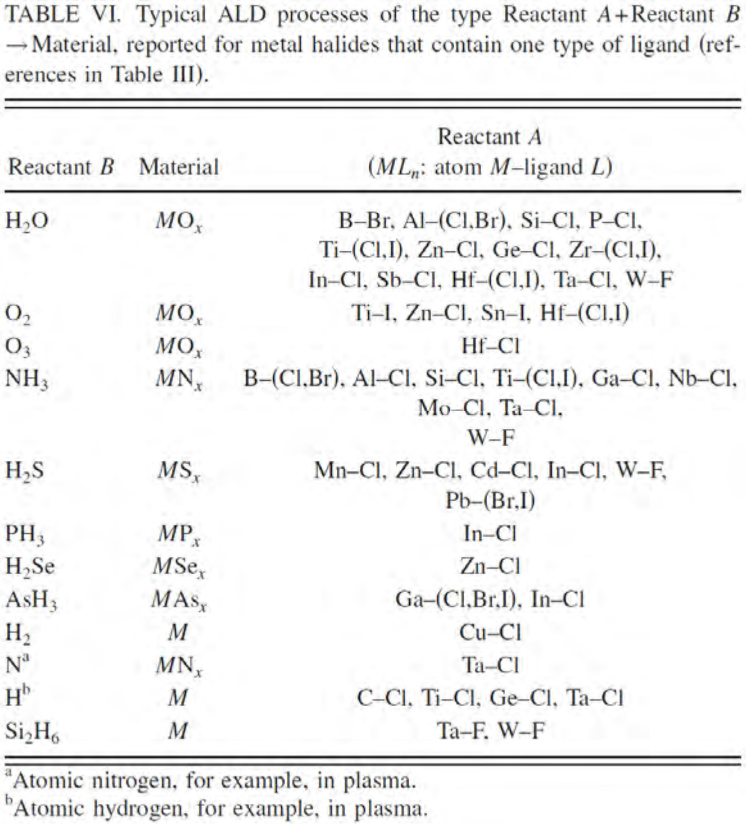


TABLE VI. Typical ALD processes of the type Reactant A+Reactant B → Material, reported for metal halides that contain one type of ligand (references in Table III).

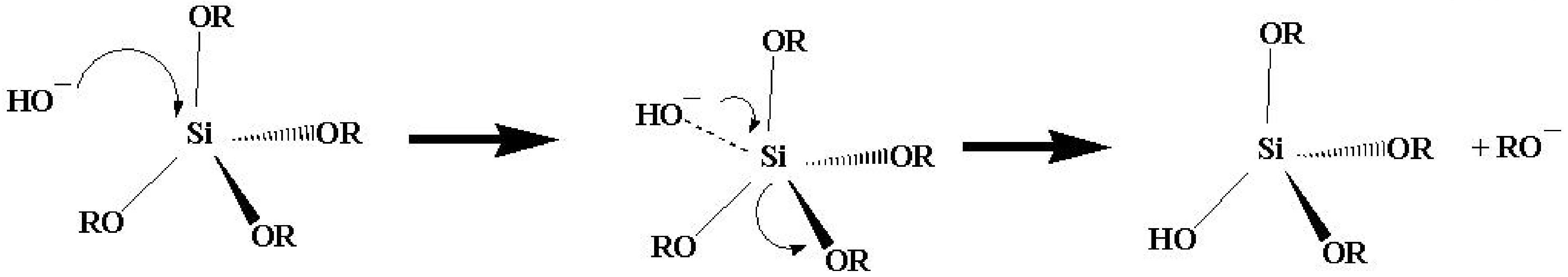
Reactant B	Material	Reactant A (ML_n: atom M–ligand L)
H_2O	MO_x	B–Br, Al–(Cl,Br), Si–Cl, P–Cl, Ti–(Cl,I), Zn–Cl, Ge–Cl, Zr–(Cl,I), In–Cl, Sb–Cl, Hf–(Cl,I), Ta–Cl, W–F
O_2	MO_x	Ti–I, Zn–Cl, Sn–I, Hf–(Cl,I)
O_3	MO_x	Hf–Cl
NH_3	MN_x	B–(Cl,Br), Al–Cl, Si–Cl, Ti–(Cl,I), Ga–Cl, Nb–Cl, Mo–Cl, Ta–Cl, W–F
H_2S	MS_x	Mn–Cl, Zn–Cl, Cd–Cl, In–Cl, W–F, Pb–(Br,I)
PH_3	MP_x	In–Cl
H_2Se	MSe_x	Zn–Cl
AsH_3	MAs_x	Ga–(Cl,Br,I), In–Cl
H_2	M	Cu–Cl
N[a]	MN_x	Ta–Cl
H[b]	M	C–Cl, Ti–Cl, Ge–Cl, Ta–Cl
Si_2H_6	M	Ta–F, W–F

[a] Atomic nitrogen, for example, in plasma.

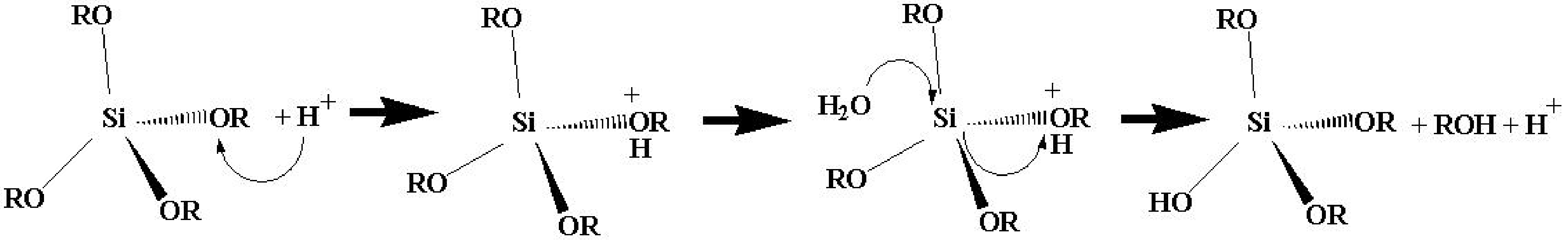
[b] Atomic hydrogen, for example, in plasma.

J. Appl. Phys. **97**, 121301 (2005)

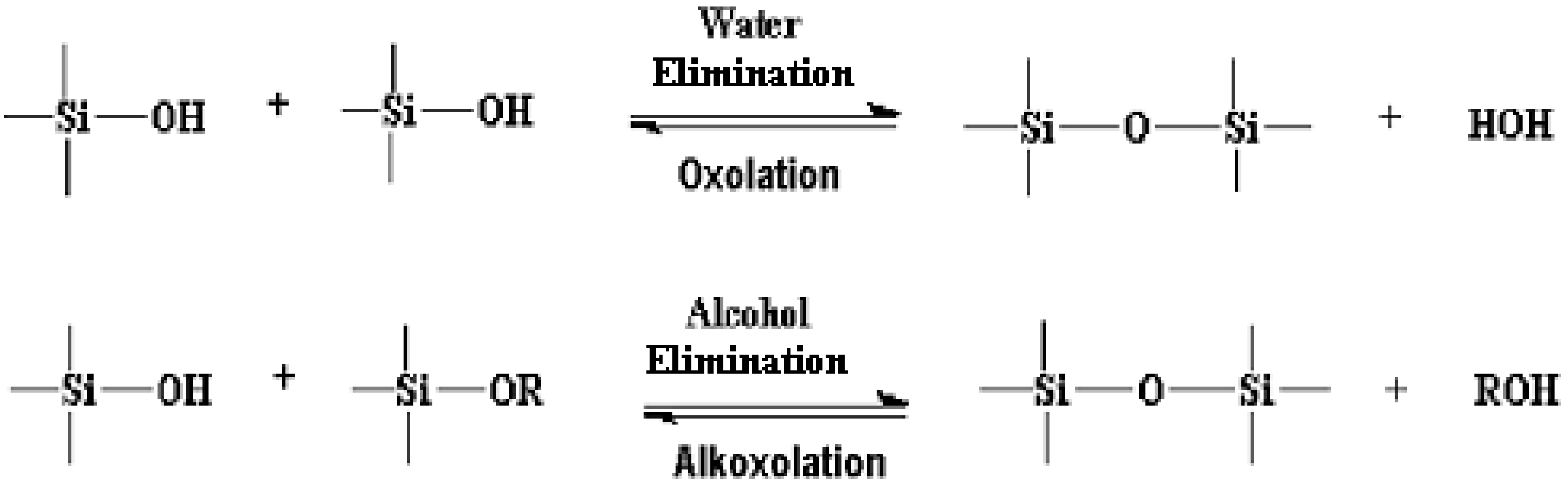
Basic hydrolysis of alkoxysilanes (S_{N2})



Acid hydrolysis of alkoxysilanes (proton assisted S_{N1})



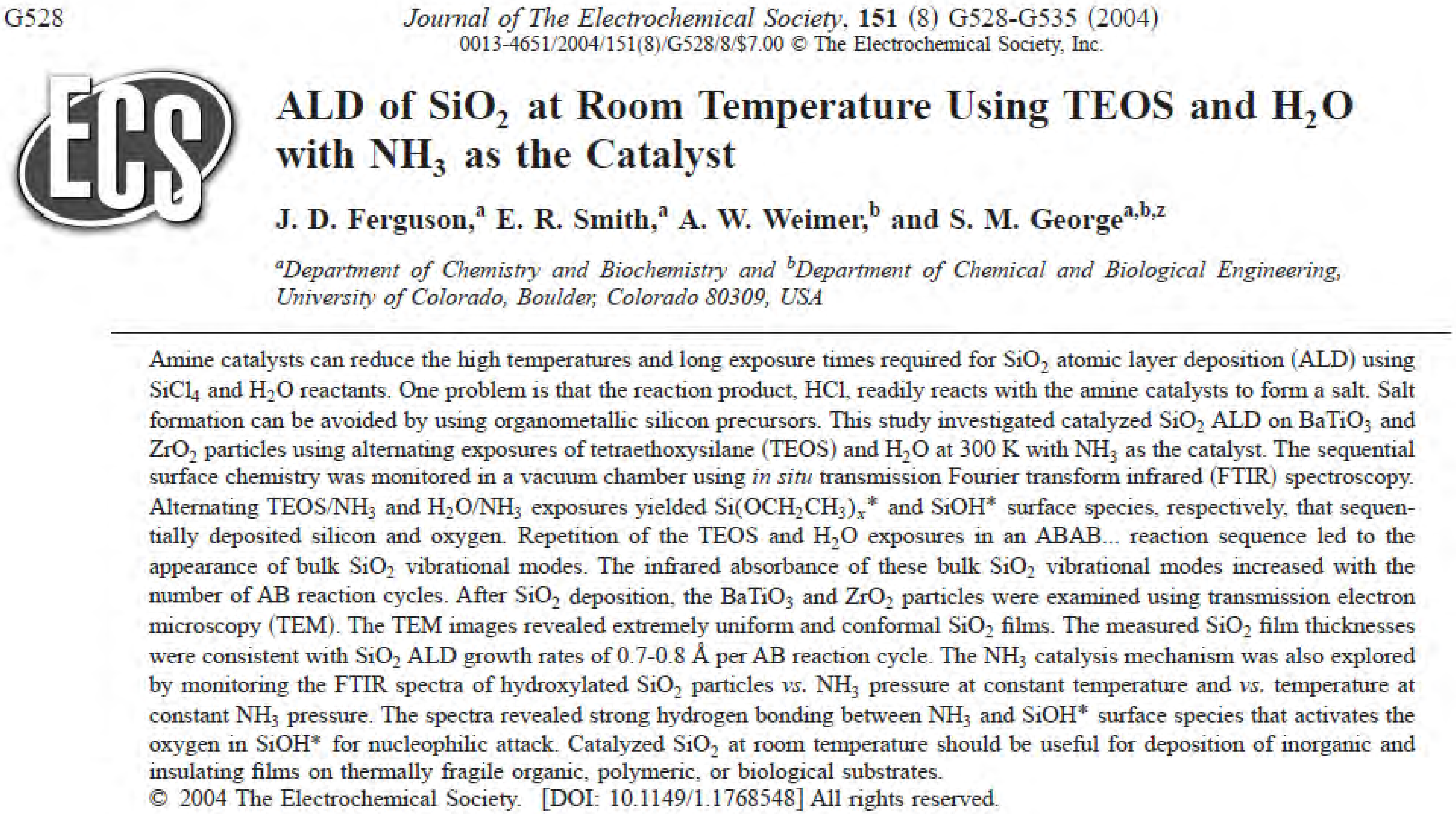
Polycondensation



$$\equiv Si{-}OH + HO{-}Si\equiv \underset{\text{Oxolation}}{\overset{\text{Water Elimination}}{\rightleftharpoons}} \equiv Si{-}O{-}Si\equiv + HOH$$

$$\equiv Si{-}OH + RO{-}Si\equiv \underset{\text{Alkoxolation}}{\overset{\text{Alcohol Elimination}}{\rightleftharpoons}} \equiv Si{-}O{-}Si\equiv + ROH$$

Silica Growth in ALD: Base Catalyzed



G528 *Journal of The Electrochemical Society*, **151** (8) G528-G535 (2004)
0013-4651/2004/151(8)/G528/8/$7.00 © The Electrochemical Society, Inc.

ALD of SiO_2 at Room Temperature Using TEOS and H_2O with NH_3 as the Catalyst

J. D. Ferguson,[a] E. R. Smith,[a] A. W. Weimer,[b] and S. M. George[a,b,z]

[a]Department of Chemistry and Biochemistry and [b]Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309, USA

Amine catalysts can reduce the high temperatures and long exposure times required for SiO_2 atomic layer deposition (ALD) using $SiCl_4$ and H_2O reactants. One problem is that the reaction product, HCl, readily reacts with the amine catalysts to form a salt. Salt formation can be avoided by using organometallic silicon precursors. This study investigated catalyzed SiO_2 ALD on $BaTiO_3$ and ZrO_2 particles using alternating exposures of tetraethoxysilane (TEOS) and H_2O at 300 K with NH_3 as the catalyst. The sequential surface chemistry was monitored in a vacuum chamber using *in situ* transmission Fourier transform infrared (FTIR) spectroscopy. Alternating TEOS/NH_3 and H_2O/NH_3 exposures yielded $Si(OCH_2CH_3)_x{}^*$ and SiOH* surface species, respectively, that sequentially deposited silicon and oxygen. Repetition of the TEOS and H_2O exposures in an ABAB... reaction sequence led to the appearance of bulk SiO_2 vibrational modes. The infrared absorbance of these bulk SiO_2 vibrational modes increased with the number of AB reaction cycles. After SiO_2 deposition, the $BaTiO_3$ and ZrO_2 particles were examined using transmission electron microscopy (TEM). The TEM images revealed extremely uniform and conformal SiO_2 films. The measured SiO_2 film thicknesses were consistent with SiO_2 ALD growth rates of 0.7-0.8 Å per AB reaction cycle. The NH_3 catalysis mechanism was also explored by monitoring the FTIR spectra of hydroxylated SiO_2 particles *vs.* NH_3 pressure at constant temperature and *vs.* temperature at constant NH_3 pressure. The spectra revealed strong hydrogen bonding between NH_3 and SiOH* surface species that activates the oxygen in SiOH* for nucleophilic attack. Catalyzed SiO_2 at room temperature should be useful for deposition of inorganic and insulating films on thermally fragile organic, polymeric, or biological substrates.

Sol–Gel Chemistry and Atomic Layer Deposition

Guylhaine Clavel, Catherine Marichy, and Nicola Pinna

Atomic Layer Deposition of Nanostructured Materials, First Edition. Edited by Nicola Pinna and Mato Knez.

Silica Growth by ALD: "Self-Catalyzed"

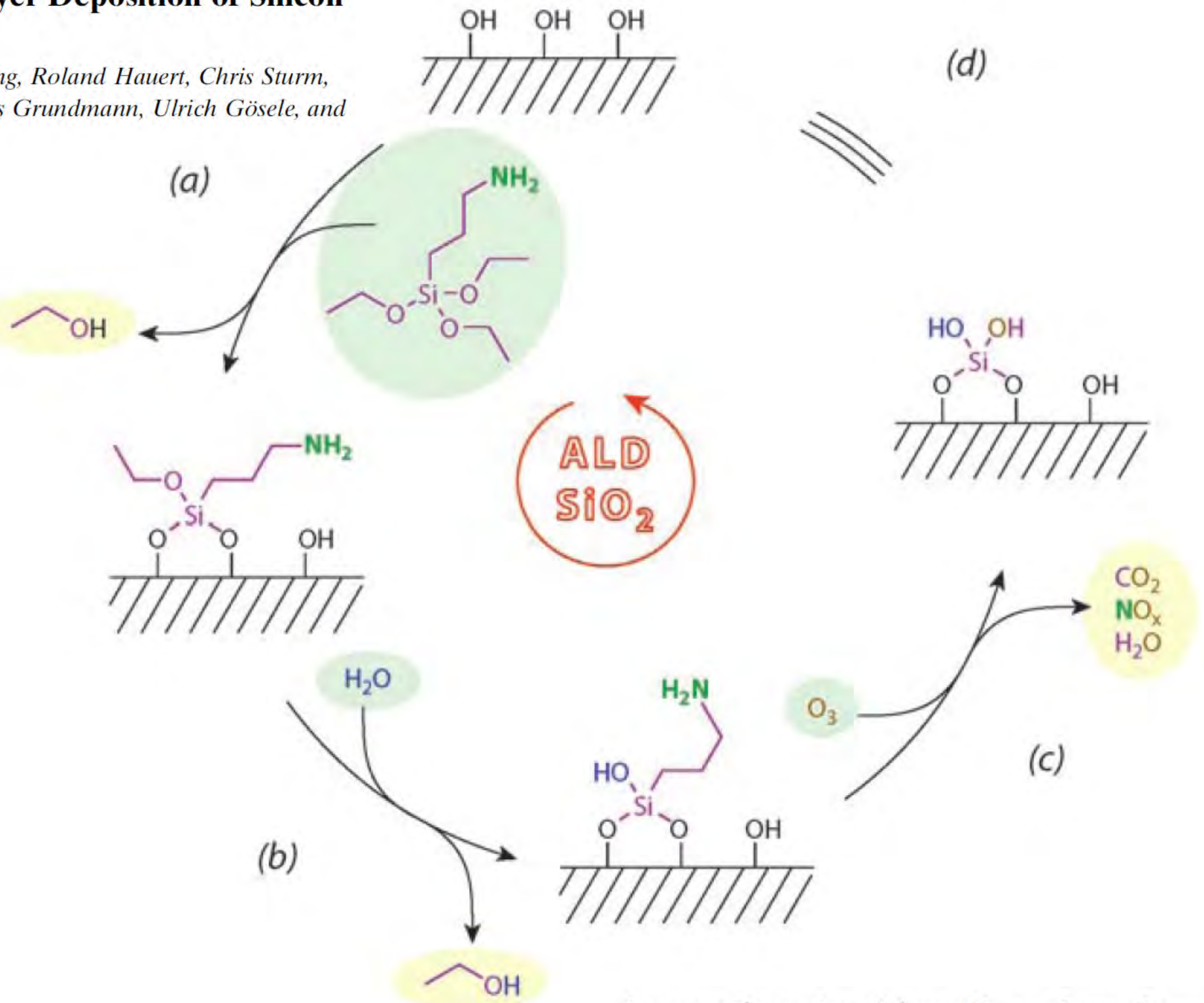
A Practical, Self-Catalytic, Atomic Layer Deposition of Silicon Dioxide**

Julien Bachmann, Robert Zierold, Yuen Tung Chong, Roland Hauert, Chris Sturm, Rüdiger Schmidt-Grund, Bernd Rheinländer, Marius Grundmann, Ulrich Gösele, and Kornelius Nielsch**

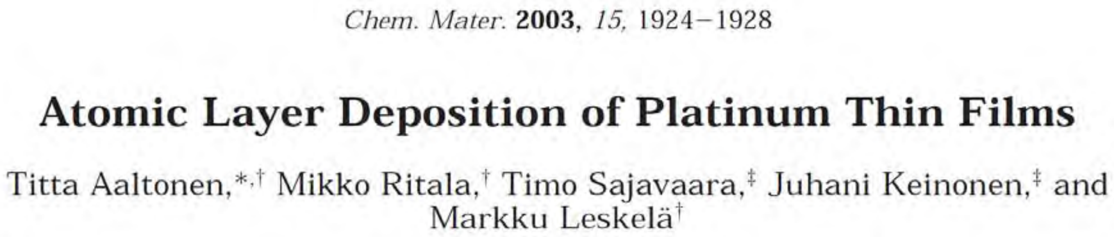
a) Anchoring: surface hydroxy groups cleave Si-OEt bonds of the silane under self-catalysis by the pendent amino group (green), causing chemisorption

b) Hydrolysis: remaining ethoxy groups are removed self-catalytically

c) Oxidation: the aminoalkyl arm is removed by ozone



Angew. Chem. Int. Ed. **2008**, 47, 6177–6179

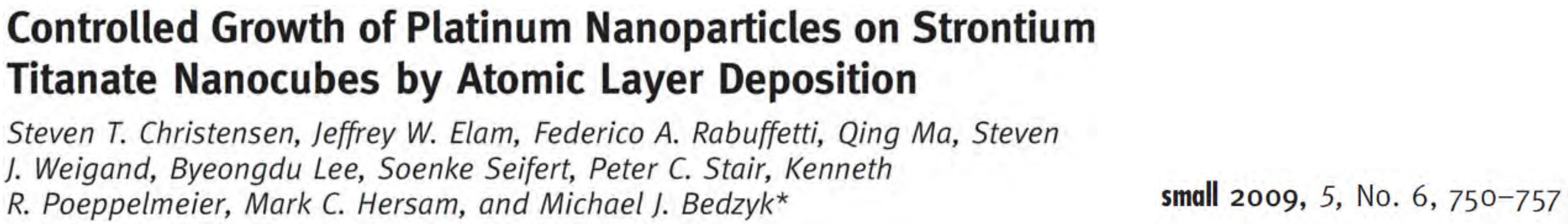


Chem. Mater. **2003**, *15*, 1924–1928

Atomic Layer Deposition of Platinum Thin Films

Titta Aaltonen,*,† Mikko Ritala,† Timo Sajavaara,‡ Juhani Keinonen,‡ and Markku Leskelä†

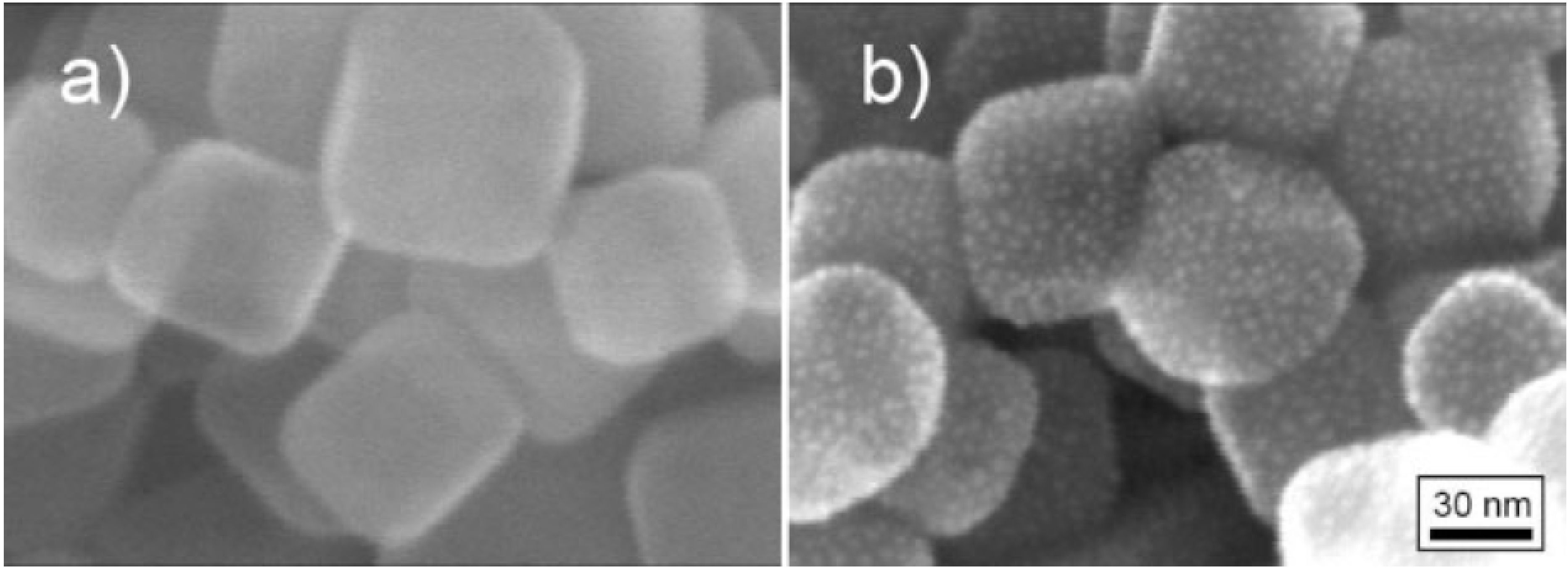
Platinum thin films were grown at 300 °C by atomic layer deposition (ALD) using (methylcyclopentadienyl)trimethylplatinum ($MeCpPtMe_3$) and oxygen as precursors. The films had excellent uniformity, low resistivity, and low-impurity contents.



Controlled Growth of Platinum Nanoparticles on Strontium Titanate Nanocubes by Atomic Layer Deposition

*Steven T. Christensen, Jeffrey W. Elam, Federico A. Rabuffetti, Qing Ma, Steven J. Weigand, Byeongdu Lee, Soenke Seifert, Peter C. Stair, Kenneth R. Poeppelmeier, Mark C. Hersam, and Michael J. Bedzyk**

small 2009, *5*, No. 6, 750–757



Plasma-enhanced ALD

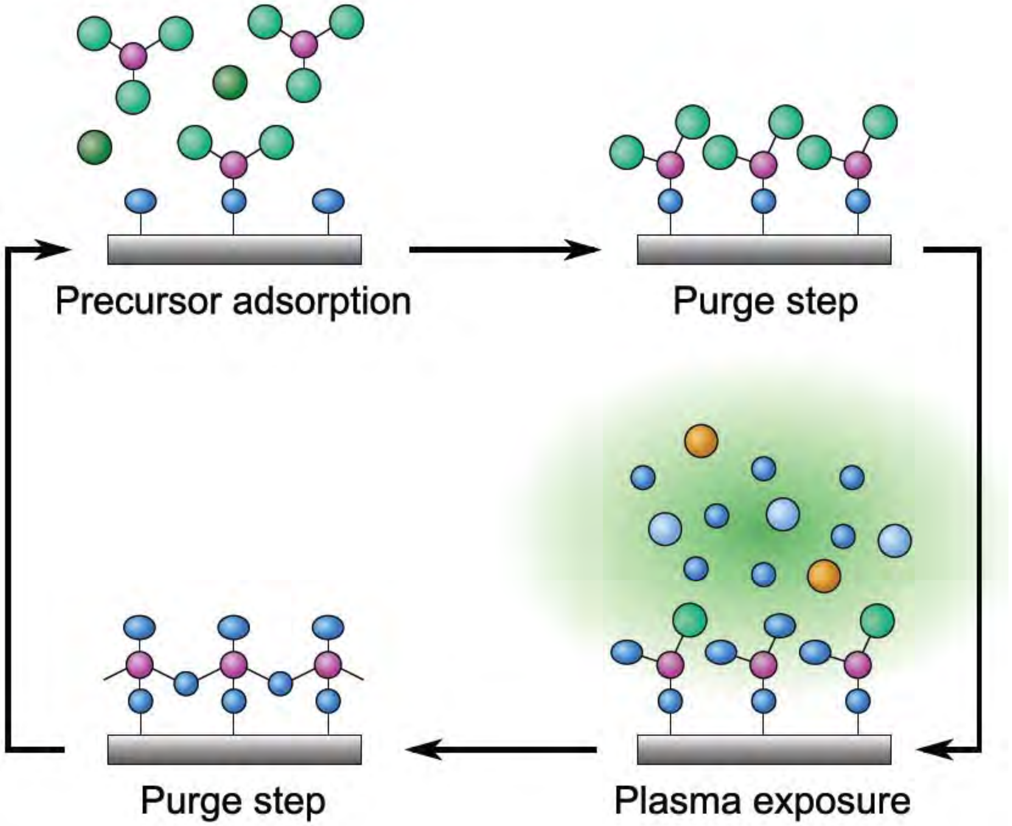


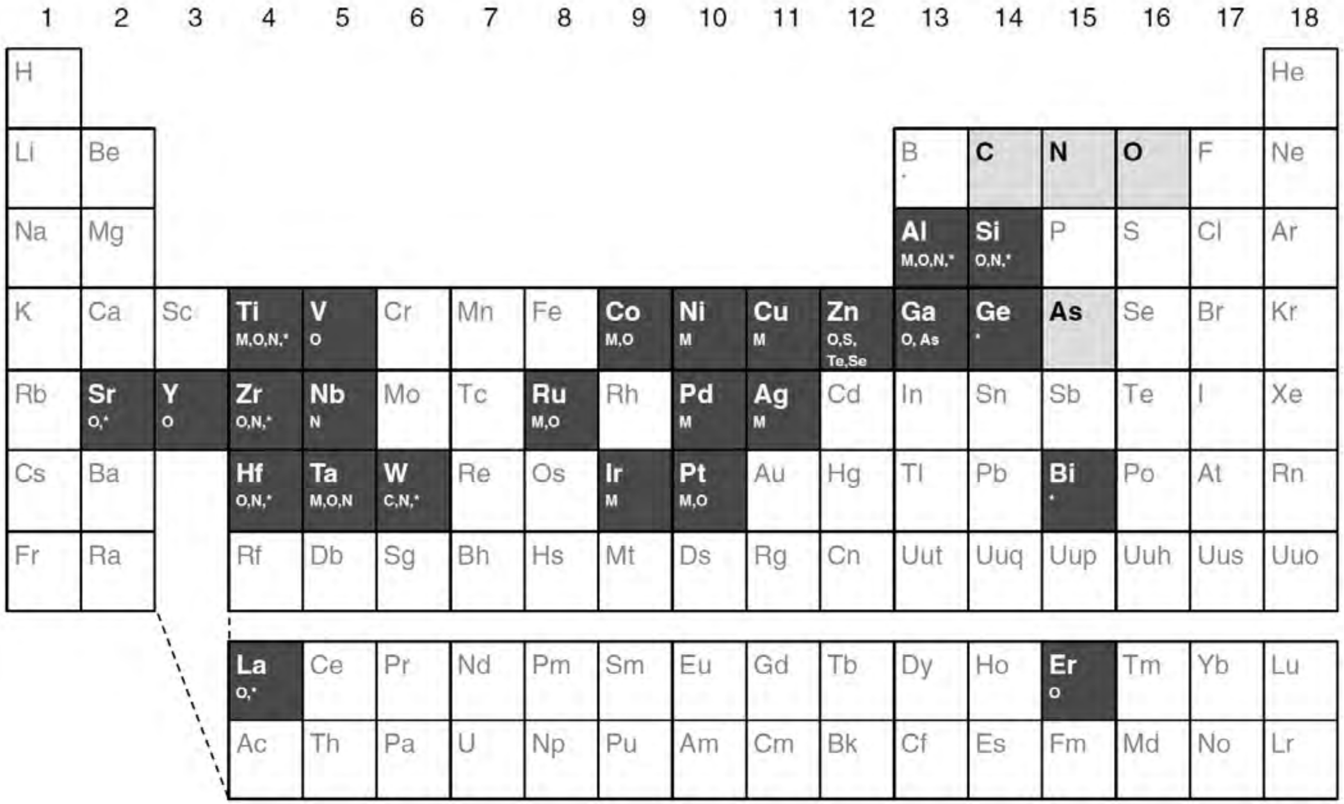
Figure 7.1 Schematic representation of plasma ALD. During the coreactant step of the cycle, the surface is exposed to species generated by a plasma.

7
Plasma Atomic Layer Deposition

Erwin Kessels, Harald Profijt, Stephen Potts, and Richard van de Sanden

Atomic Layer Deposition of Nanostructured Materials, First Edition. Edited by Nicola Pinna and Mato Knez.

Plasma-enhanced ALD



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B *	**C**	**N**	**O**	F	Ne
Na	Mg											**Al** M,O,N,*	**Si** O,N,*	P	S	Cl	Ar
K	Ca	Sc	**Ti** M,O,N,*	**V** O	Cr	Mn	Fe	**Co** M,O	**Ni** M	**Cu** M	**Zn** O,S, Te,Se	**Ga** O, As	**Ge** *	**As**	Se	Br	Kr
Rb	**Sr** O,*	**Y** O	**Zr** O,N,*	**Nb** N	Mo	Tc	**Ru** M,O	Rh	**Pd** M	**Ag** M	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		**Hf** O,N,*	**Ta** M,O,N	**W** C,N,*	Re	Os	**Ir** M	**Pt** M,O	Au	Hg	Tl	Pb	**Bi** *	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo
			La O,*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	**Er** O	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 7.3 Periodic table showing the elements (dark background) that have been part of films synthesized by plasma ALD. "M" means that the pure elements were deposited; compounds with oxygen, nitrogen, and other elements are indicated by their symbols ("O", "N", etc.). Asterisks denote ternary or other compounds.

7

Plasma Atomic Layer Deposition

Erwin Kessels, Harald Profijt, Stephen Potts, and Richard van de Sanden

Atomic Layer Deposition of Nanostructured Materials, First Edition. Edited by Nicola Pinna and Mato Knez.

Molecular Layer Deposition

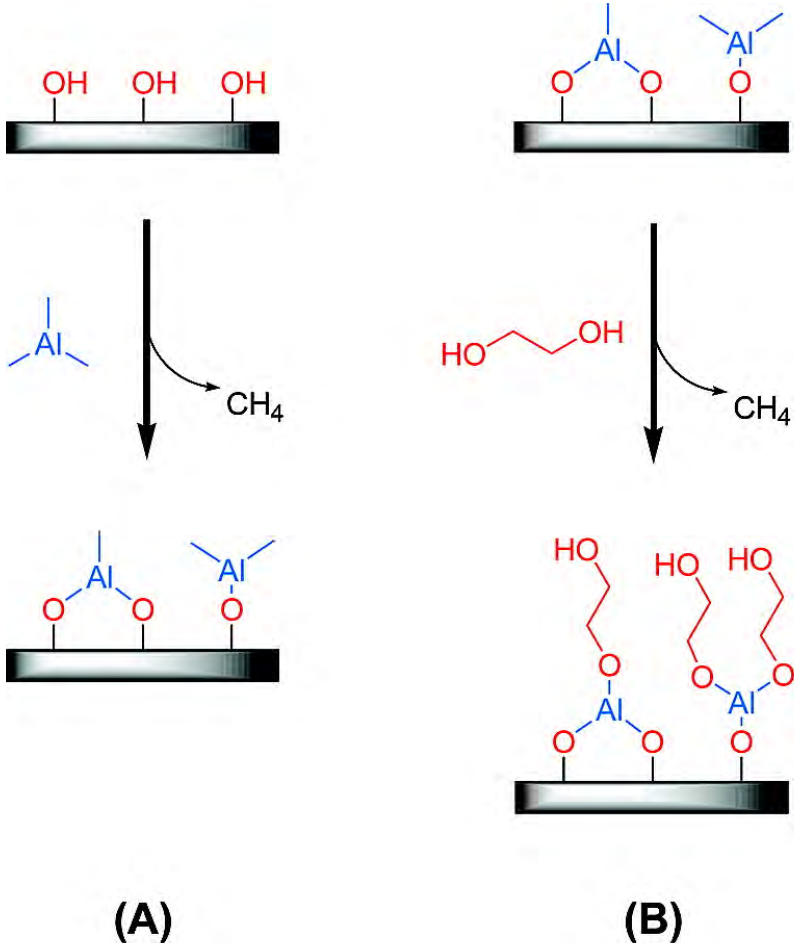


Illustration of surface chemistry for poly(aluminum ethylene glycol) alucone MLD using TMA and EG as reactants.

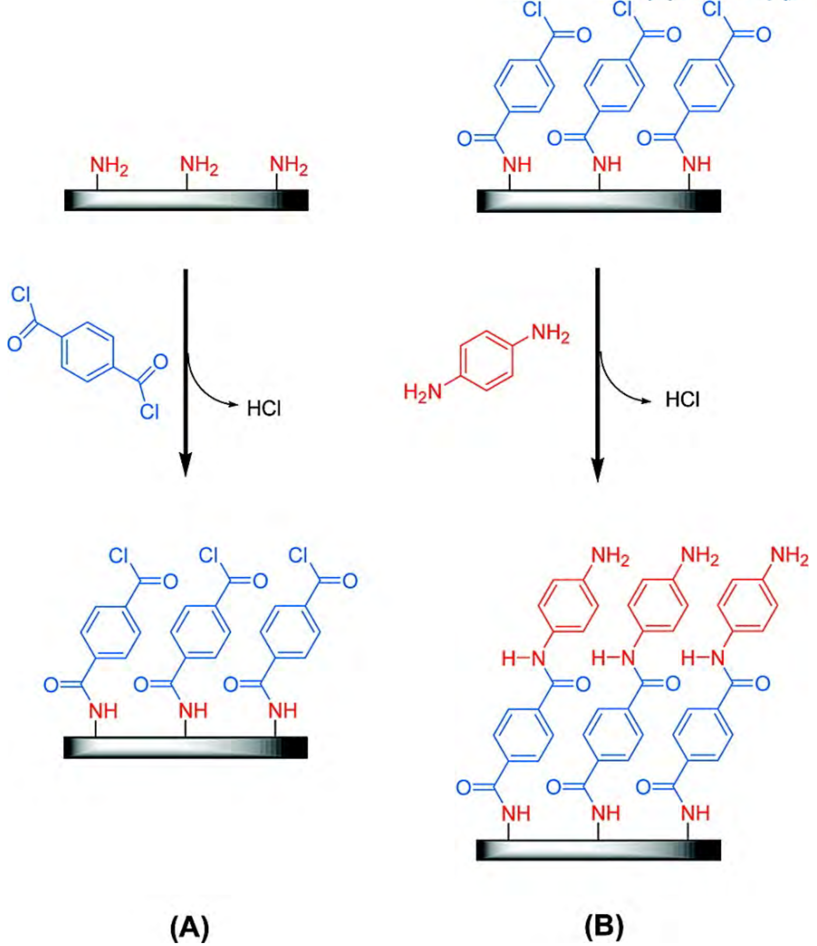


Illustration of surface chemistry for PPTA MLD using terephthaloyl chloride and p-phenylenediamine as reactants.

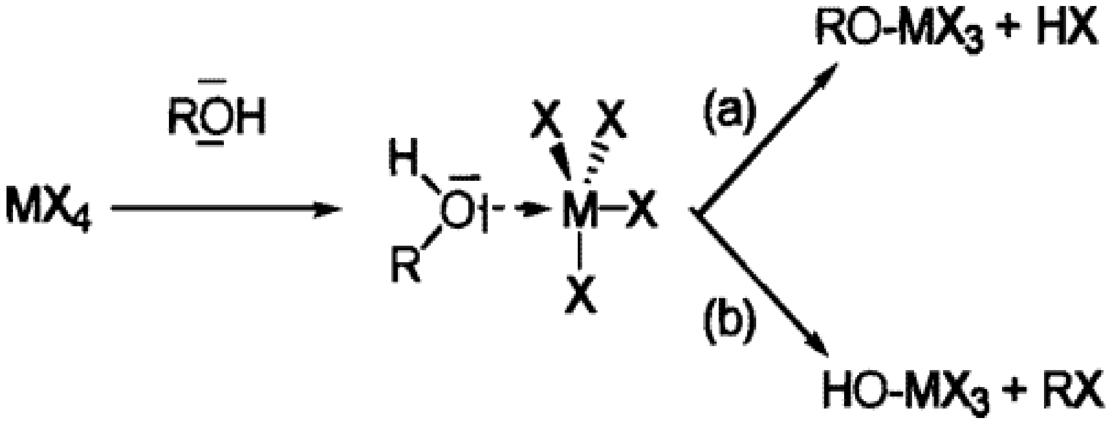
S.M. George, B. Yoon, A.A. Dameron; *Acc. Chem. Res.* **2009**, 42, 498-508.

Nonaqueous Sol-Gel Routes to Oxides

1. Nonhydrolytic Hydroxylation Reactions

(Formation of M-OH species)

Reaction of alcohols with metal halides:



1) Coordination of the alcohol to the metal centre

2) a) Formation of metal alkoxide under elimination of HX

b) Formation of hydroxyl group and elimination of alkyl halide RX (if R is an electron-donor substituent, the nucleophilic attack of the chloride on the carbon group is favored)

A. Vioux: Chem. Mater. **1997**, 9, 2292-2299

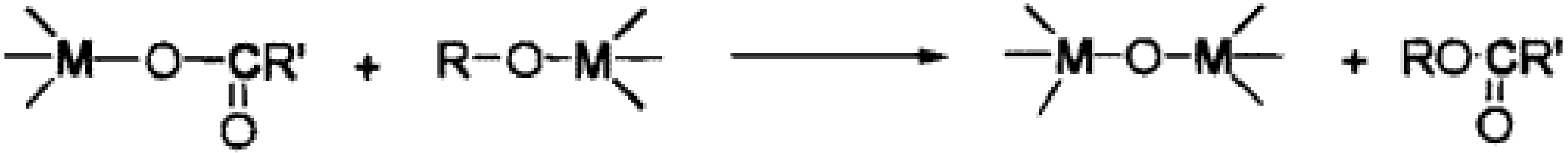
Nonaqueous Sol-Gel Routes to Oxides

Aprotic Condensation Reactions

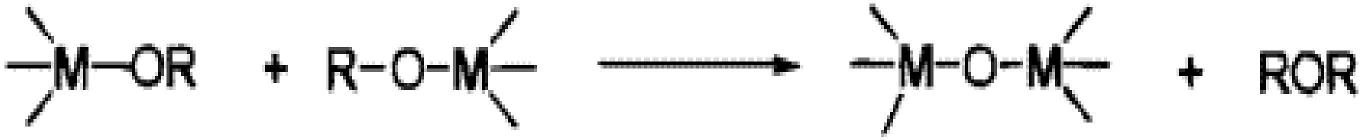
(M-O-M Bond Formation)

Reaction between metal alkoxides and metal halides under alkyl halide elimination

Reaction between metal acetates and metal alkoxides under ester elimination

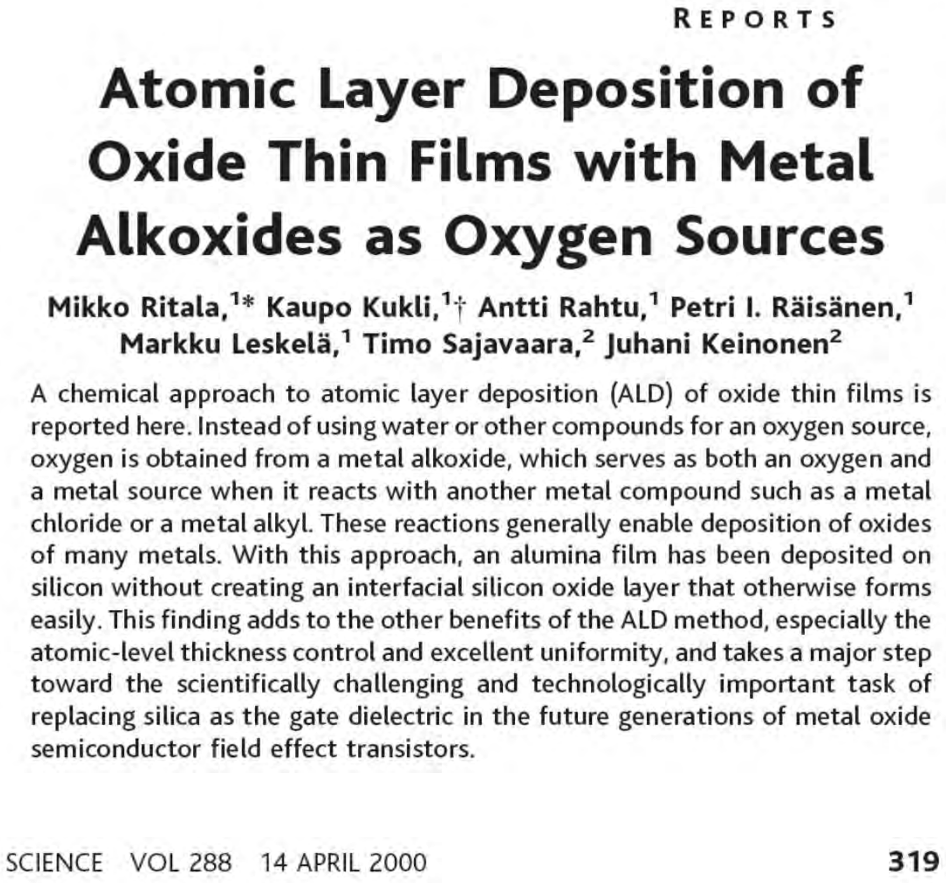


Reaction between two metal alkoxides under ether elimination



A. Vioux: Chem. Mater. **1997**, 9, 2292-2299

Alkyl Halide Elimination



Atomic Layer Deposition of Oxide Thin Films with Metal Alkoxides as Oxygen Sources

Mikko Ritala,[1]* Kaupo Kukli,[1]† Antti Rahtu,[1] Petri I. Räisänen,[1] Markku Leskelä,[1] Timo Sajavaara,[2] Juhani Keinonen[2]

A chemical approach to atomic layer deposition (ALD) of oxide thin films is reported here. Instead of using water or other compounds for an oxygen source, oxygen is obtained from a metal alkoxide, which serves as both an oxygen and a metal source when it reacts with another metal compound such as a metal chloride or a metal alkyl. These reactions generally enable deposition of oxides of many metals. With this approach, an alumina film has been deposited on silicon without creating an interfacial silicon oxide layer that otherwise forms easily. This finding adds to the other benefits of the ALD method, especially the atomic-level thickness control and excellent uniformity, and takes a major step toward the scientifically challenging and technologically important task of replacing silica as the gate dielectric in the future generations of metal oxide semiconductor field effect transistors.

SCIENCE VOL 288 14 APRIL 2000 319

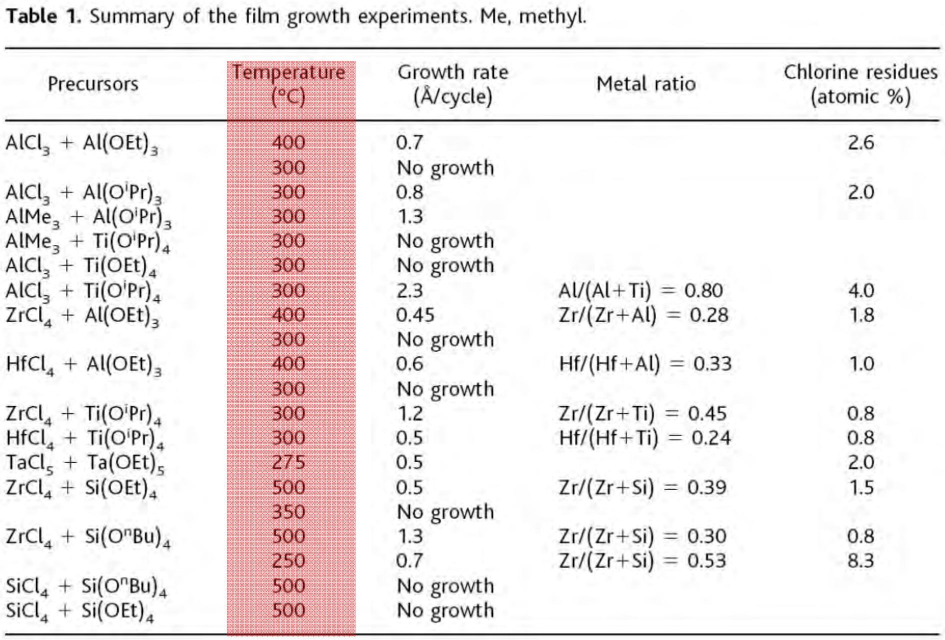


Table 1. Summary of the film growth experiments. Me, methyl.

Precursors	Temperature (°C)	Growth rate (Å/cycle)	Metal ratio	Chlorine residues (atomic %)
$AlCl_3$ + $Al(OEt)_3$	400	0.7		2.6
	300	No growth		
$AlCl_3$ + $Al(O^iPr)_3$	300	0.8		2.0
$AlMe_3$ + $Al(O^iPr)_3$	300	1.3		
$AlMe_3$ + $Ti(O^iPr)_4$	300	No growth		
$AlCl_3$ + $Ti(OEt)_4$	300	No growth		
$AlCl_3$ + $Ti(O^iPr)_4$	300	2.3	Al/(Al+Ti) = 0.80	4.0
$ZrCl_4$ + $Al(OEt)_3$	400	0.45	Zr/(Zr+Al) = 0.28	1.8
	300	No growth		
$HfCl_4$ + $Al(OEt)_3$	400	0.6	Hf/(Hf+Al) = 0.33	1.0
	300	No growth		
$ZrCl_4$ + $Ti(O^iPr)_4$	300	1.2	Zr/(Zr+Ti) = 0.45	0.8
$HfCl_4$ + $Ti(O^iPr)_4$	300	0.5	Hf/(Hf+Ti) = 0.24	0.8
$TaCl_5$ + $Ta(OEt)_5$	275	0.5		2.0
$ZrCl_4$ + $Si(OEt)_4$	500	0.5	Zr/(Zr+Si) = 0.39	1.5
	350	No growth		
$ZrCl_4$ + $Si(O^nBu)_4$	500	1.3	Zr/(Zr+Si) = 0.30	0.8
	250	0.7	Zr/(Zr+Si) = 0.53	8.3
$SiCl_4$ + $Si(O^nBu)_4$	500	No growth		
$SiCl_4$ + $Si(OEt)_4$	500	No growth		

Non-Aqueous Sol-Gel Routes Applied to ALD

- Metal Precursors: $Hf(OtBu)_4$, $Ti(OiPr)_4$, $VO(OPr)_3$, $Sn(OtBu)_4$
- Oxygen Sources: Carboxylic acids e.g. acetic acid
- Deposition temperature: 50 – 350 °C

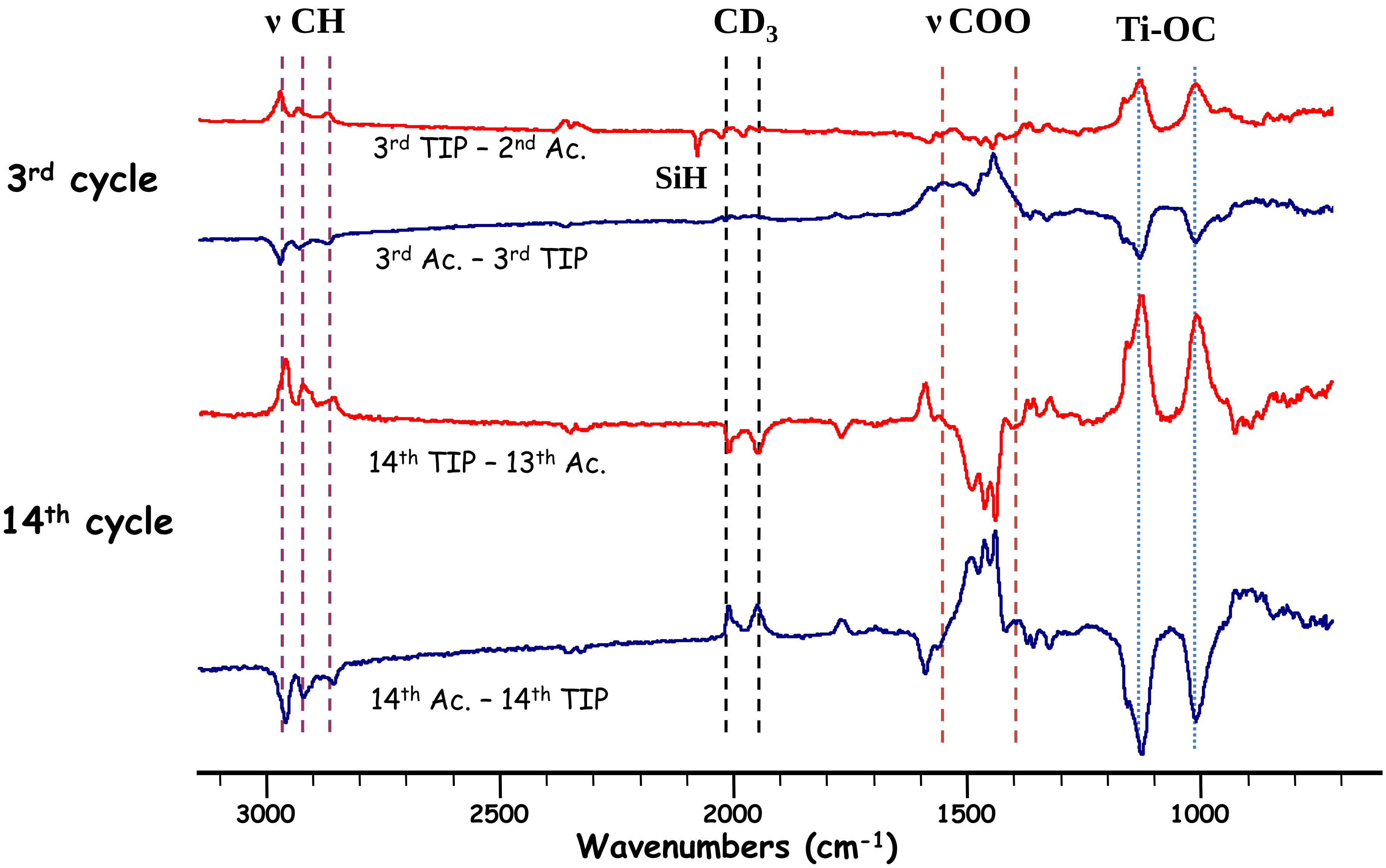
$$\boxed{\equiv M\text{-}OR' + RCOOH \rightarrow \equiv M\text{-}OOCR + R'OH \qquad \text{Eq. 1}}$$

$$\boxed{\equiv M\text{-}OOCR + M\text{-}OR' \rightarrow \equiv M\text{-}O\text{-}M\equiv + RCOOR' \qquad \text{Eq. 2}}$$

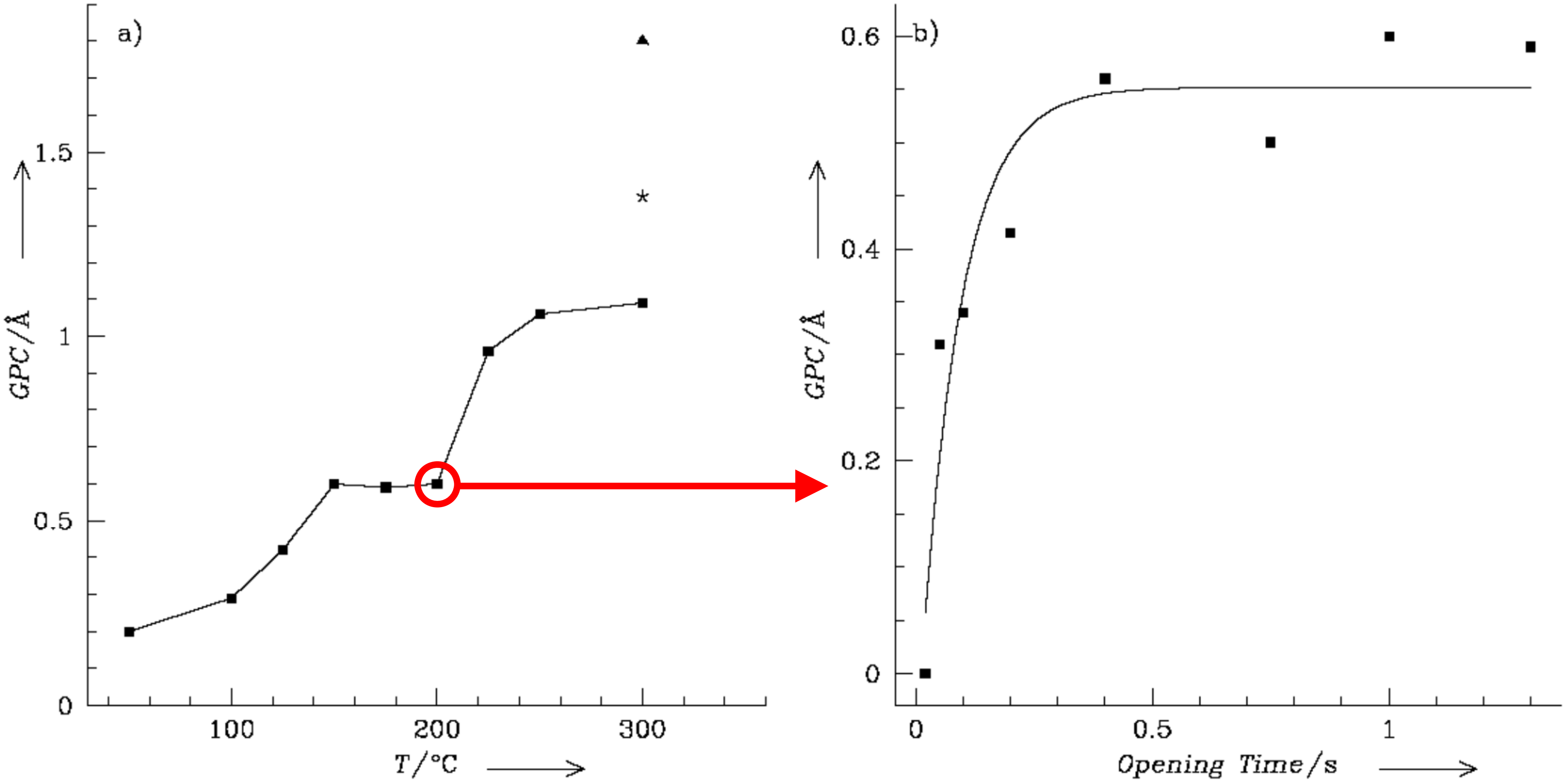
- Low oxidative character of carboxylic acids
- Large deposition temperature range
- High quality and purity of the films
- No –OH groups involved in the M-O-M bond formation

Angew. Chem. Int. Ed. **2008**, 47, 3592 - J. Phys. Chem. C **2008**, 112, 12754,
J. Mater. Chem. **2009**, 19, 454 - Adv. Funct. Mater. **2011**, 21, 658
Patent **WO 2008 098963 A2**

Difference FT-IR spectra



TiO_2



Self-limiting growth!

ALD Reactors

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Compact Reactors

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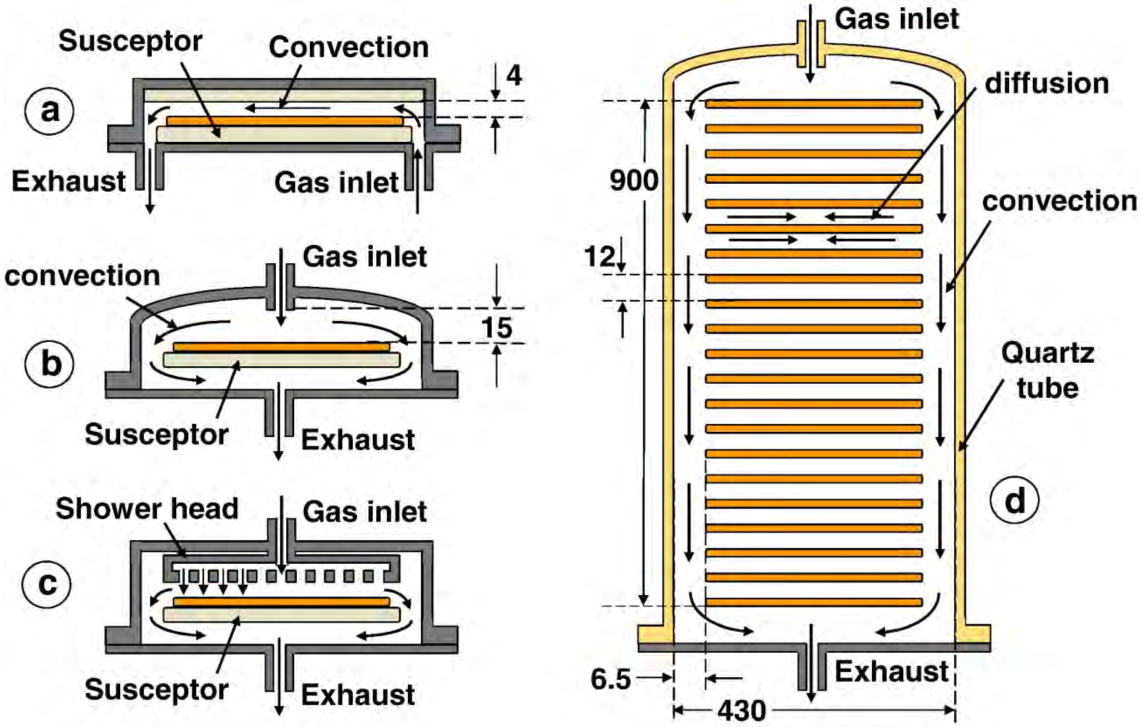
Batch Reactors



Various types of typical ALD reactor systems. a) Cross-flow reactor system based on forced flow laterally across the wafer. b) system with single injector above the center of the wafer. c) shower head system; gas is injected through an array of injectors covering the entire wafer surface. d) Vertical batch reactor: 50–150 wafers are processed simultaneously.

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E. Granneman, P. Fischer, D. Pierreux, H. Terhorst, P. Zagwijn, *Surf. Coatings Technol.* **2007**, 201, 8899

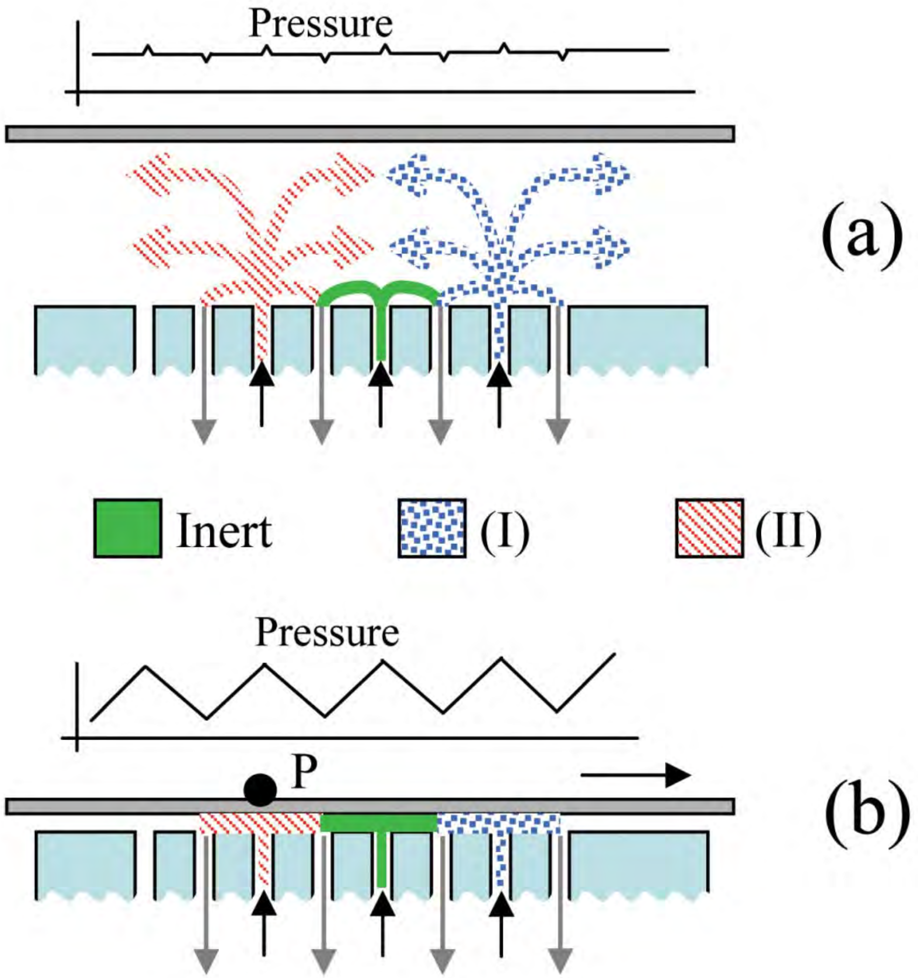


Figure 6.3 (Kodak ALD head) Side view of the spatial ALD coating head showing gas inlet slots (upward arrows) and gas exhaust slots (downward arrows). The precursors are denoted by (I) and (II), respectively. (a) A relatively large separation between the coating head and the substrate, leading to low pressure and significant gas mixing. (b) A smaller separation between the substrate and the head resulting in large pressure fields between channels [58].

58 Levy, D.H., Nelson, S. F. and Freeman, D. (2009) Oxide electronics by spatial atomic layer deposition. *J. Display Technol.*, **5** (12), 484–494.

J. Meyer and T. Riedl. Chapter 6: Low-Temperature Atomic Layer Deposition

Atomic Layer Deposition of Nanostructured Materials, First Edition. Edited by Nicola Pinna and Mato Knez.

Fluidized bed reactor

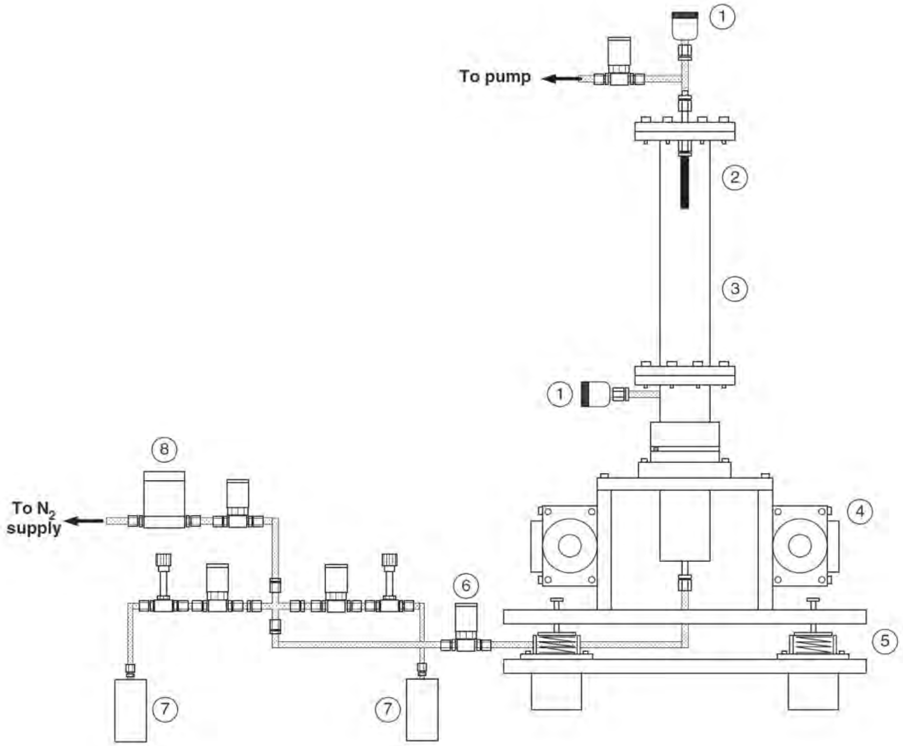


Figure 14.7 Schematic diagram of the fluidized bed reactor apparatus: (1) pressure transducers, (2) sintered metal filter, (3) reaction column, (4) vibro motors, (5) spring supports, (6) pneumatic valve, (7) reactant containers, and (8) mass flow controller. Reproduced with permission from Ref. [39].

39 Hakim, L.F., George, S.M., and Weimer, A.W. (2005) Conformal nanocoating of zirconia nanoparticles by atomic layer deposition in a fluidized bed reactor. *Nanotechnology*, **16**, S375.

Rotary reactor

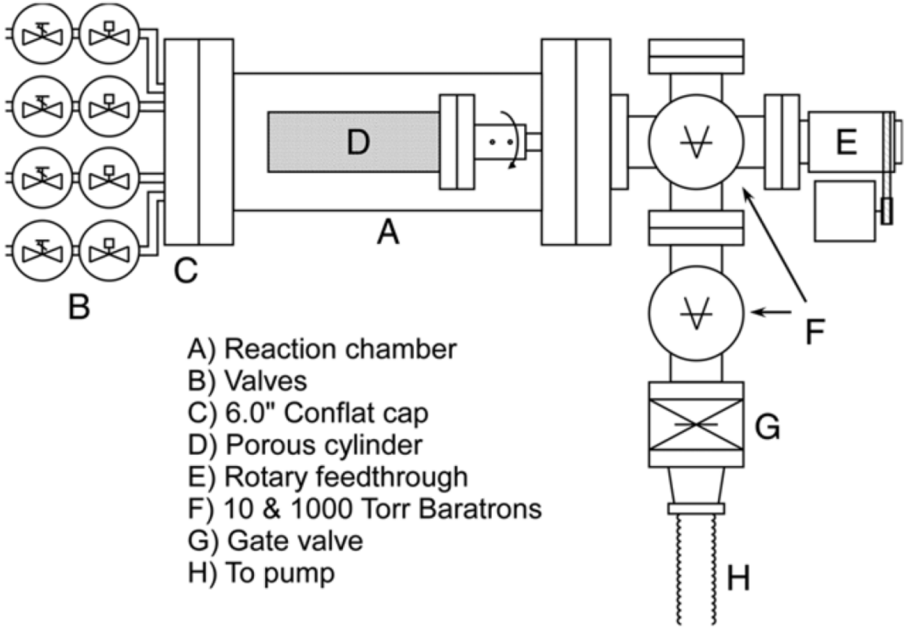


Figure 14.8 Schematic of the rotary reactor used to coat gram quantities of MWCNTs. Reproduced with permission from Ref. [33].

33 Cavanagh, A.S., Wilson, C.A., Weimer, A.W., and George, S.M. (2009) Atomic layer deposition on gram quantities of multi-walled carbon nanotubes. *Nanotechnology*, **20**, 255602.

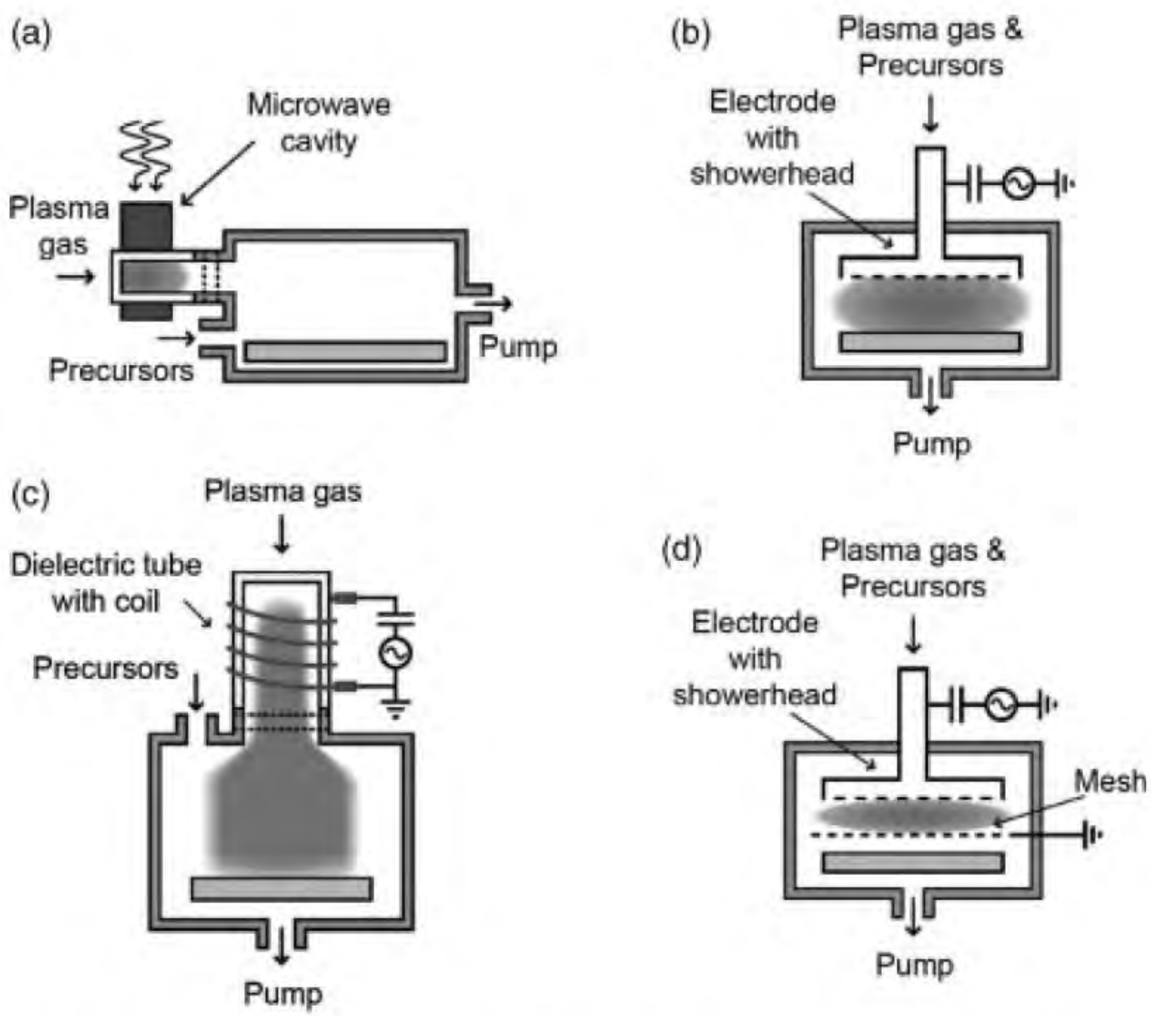


Figure 7.8 Various reactor configurations for plasma ALD: (a) radical-enhanced ALD; (b) direct plasma ALD; (c) remote plasma ALD; and (d) direct plasma reactor with mesh. The reactor layouts and plasma sources shown serve only as examples.

7
Plasma Atomic Layer Deposition

Erwin Kessels, Harald Profijt, Stephen Potts, and Richard van de Sanden

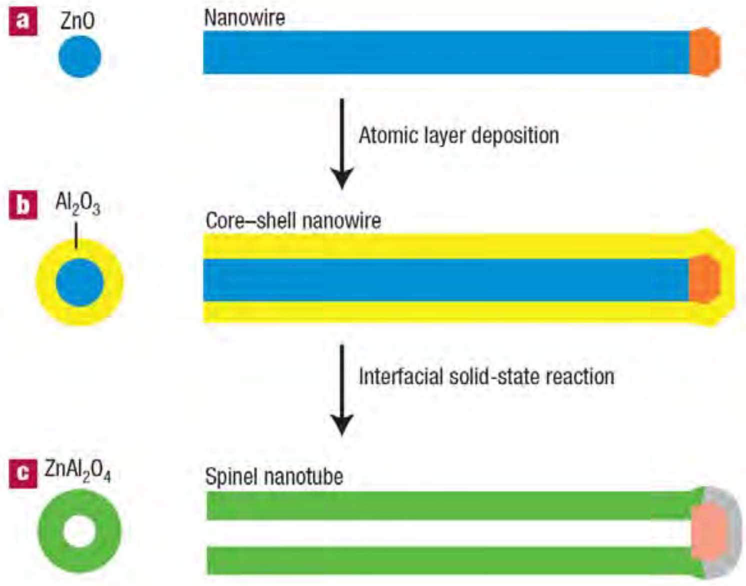
Atomic Layer Deposition of Nanostructured Materials, First Edition. Edited by Nicola Pinna and Mato Knez.

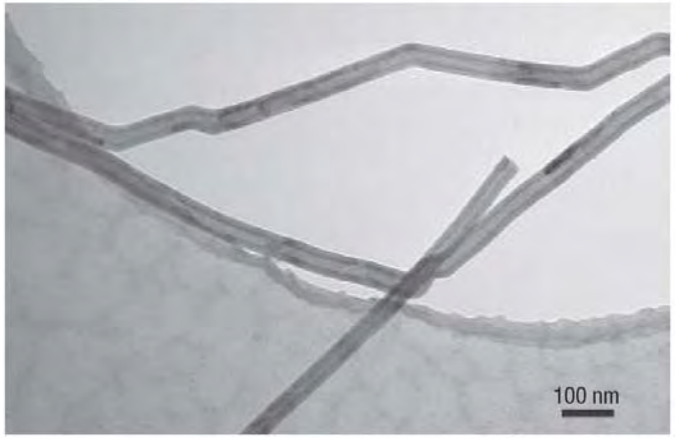
Fabrication of Nanostructures

Monocrystalline spinel nanotube fabrication based on the Kirkendall effect

HONG JIN FAN*, MATO KNEZ, ROLAND SCHOLZ, KORNELIUS NIELSCH, ECKHARD PIPPEL, DIETRICH HESSE, MARGIT ZACHARIAS† AND ULRICH GÖSELE

Nature Mater. 2006, 5, 627.





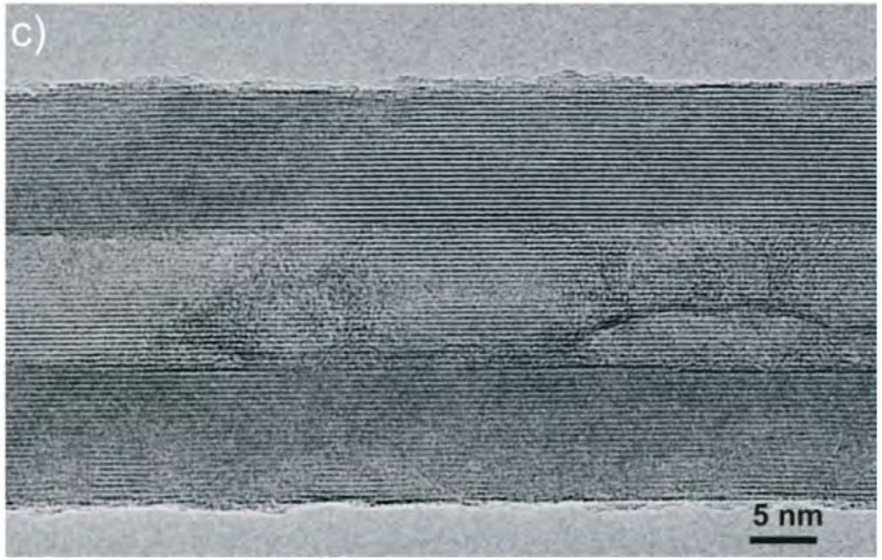


Figure 4. Schematics of the formation process of $ZnAl_2O_4$ spinel nanotubes. a) Single crystal ZnO nanowires are grown via the vapor-liquid-solid mechanism using Au nanoparticles as catalyst. b) The nanowires are coated with a uniform layer of Al_2O_3 by atomic layer deposition, forming core–shell ZnO-Al_2O_3 nanowires. c) Annealing the core–shell nanowires leads to the formation of $ZnAl_2O_4$ nanotubes via a spinel-forming interfacial solid-state reaction involving the Kirkendall effect. Reproduced with permission from [39]. Copyright 2006 Nature Publishing Group.

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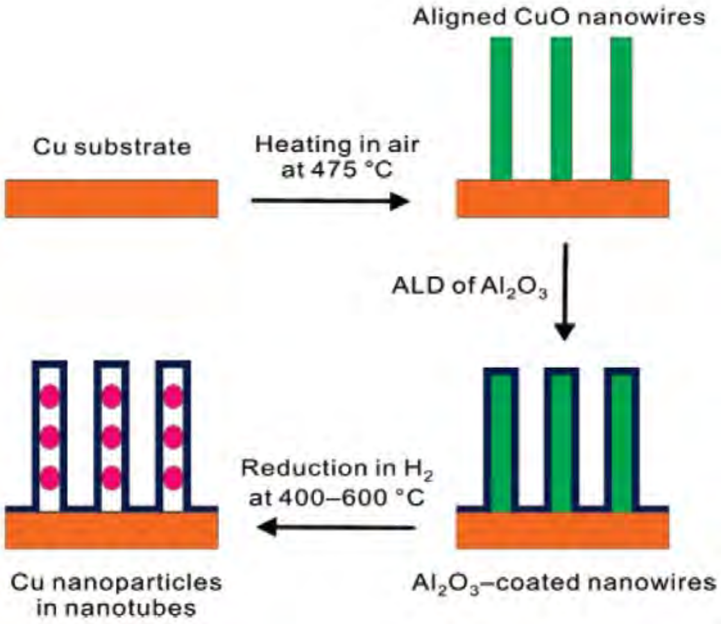
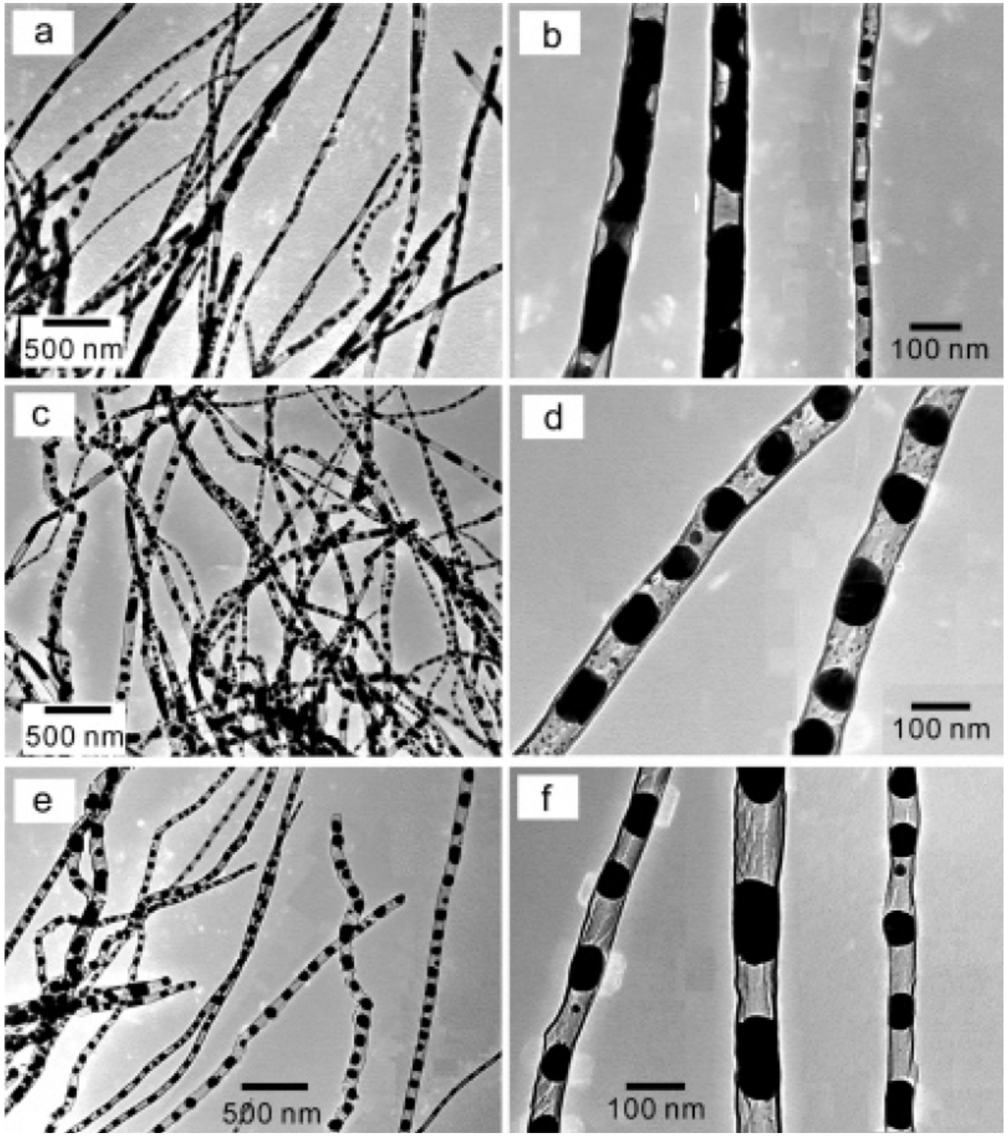
2008
Vol. 8, No. 1
114−118

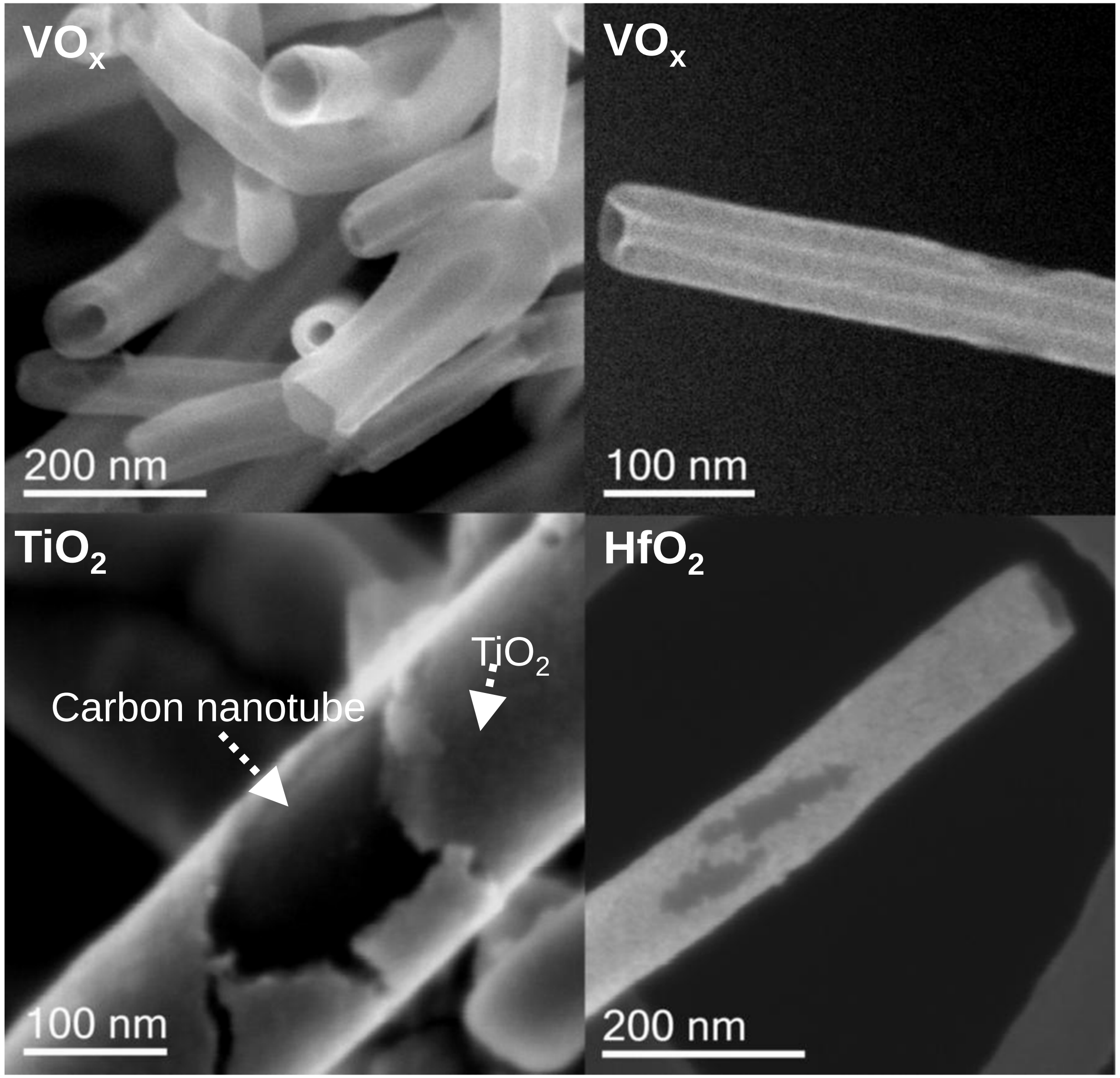
Rayleigh-Instability-Induced Metal Nanoparticle Chains Encapsulated in Nanotubes Produced by Atomic Layer Deposition

Yong Qin, Seung-Mo Lee, Anlian Pan, Ulrich Gösele, and Mato Knez*





Conformal coating of carbon nanotubes

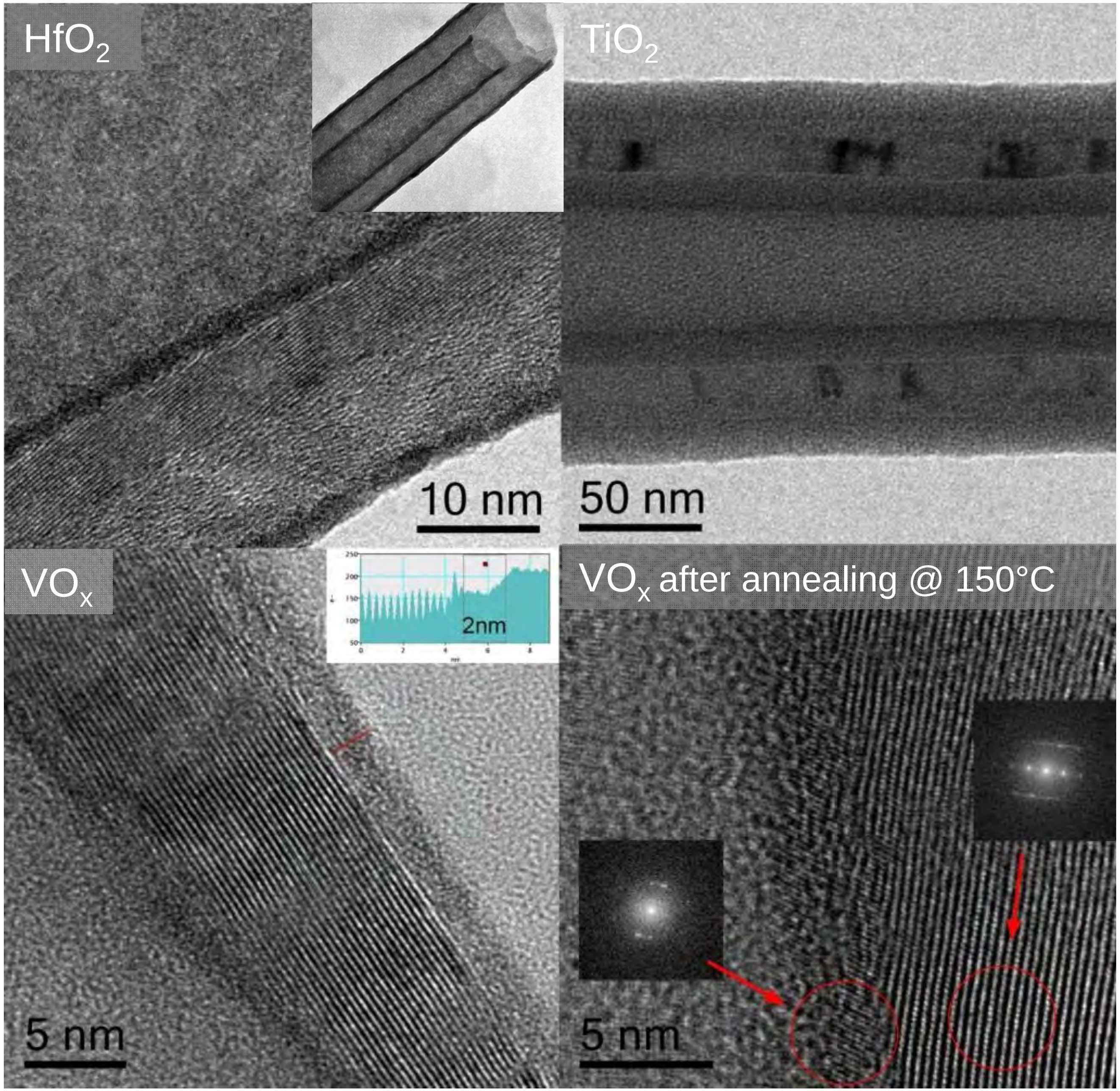


Characterization:
SEM

SEM images recorded at different acceleration voltages using SE and BSE detectors prove that the tubes are coated on the in- and outside surfaces.

Nano Lett. **2008**, 8, 4201 - Phys. Chem. Chem. Phys. **2009**, 11, 3615 - Adv. Funct. Mater. **2011**, 21, 658

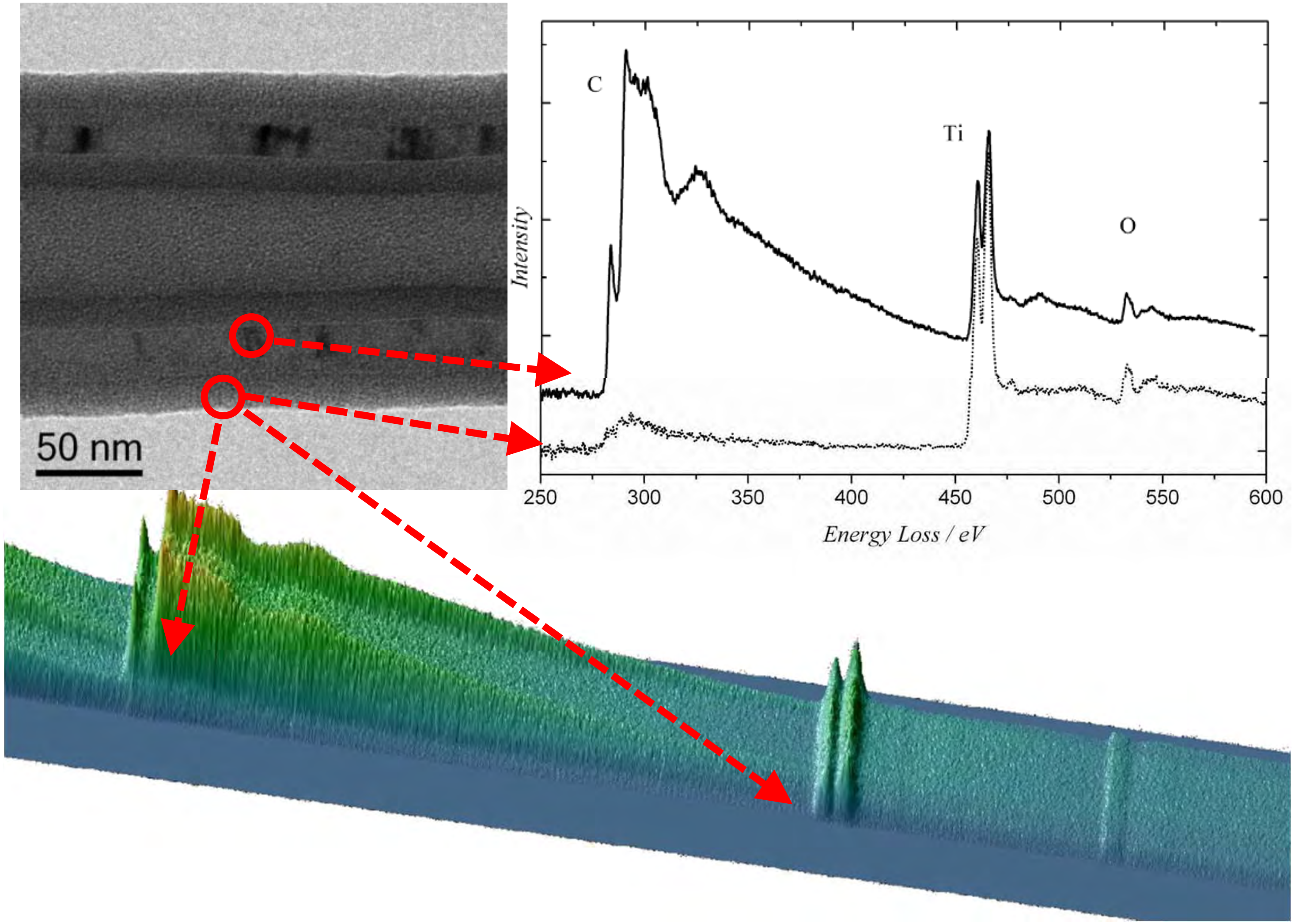
Characterization: HRTEM



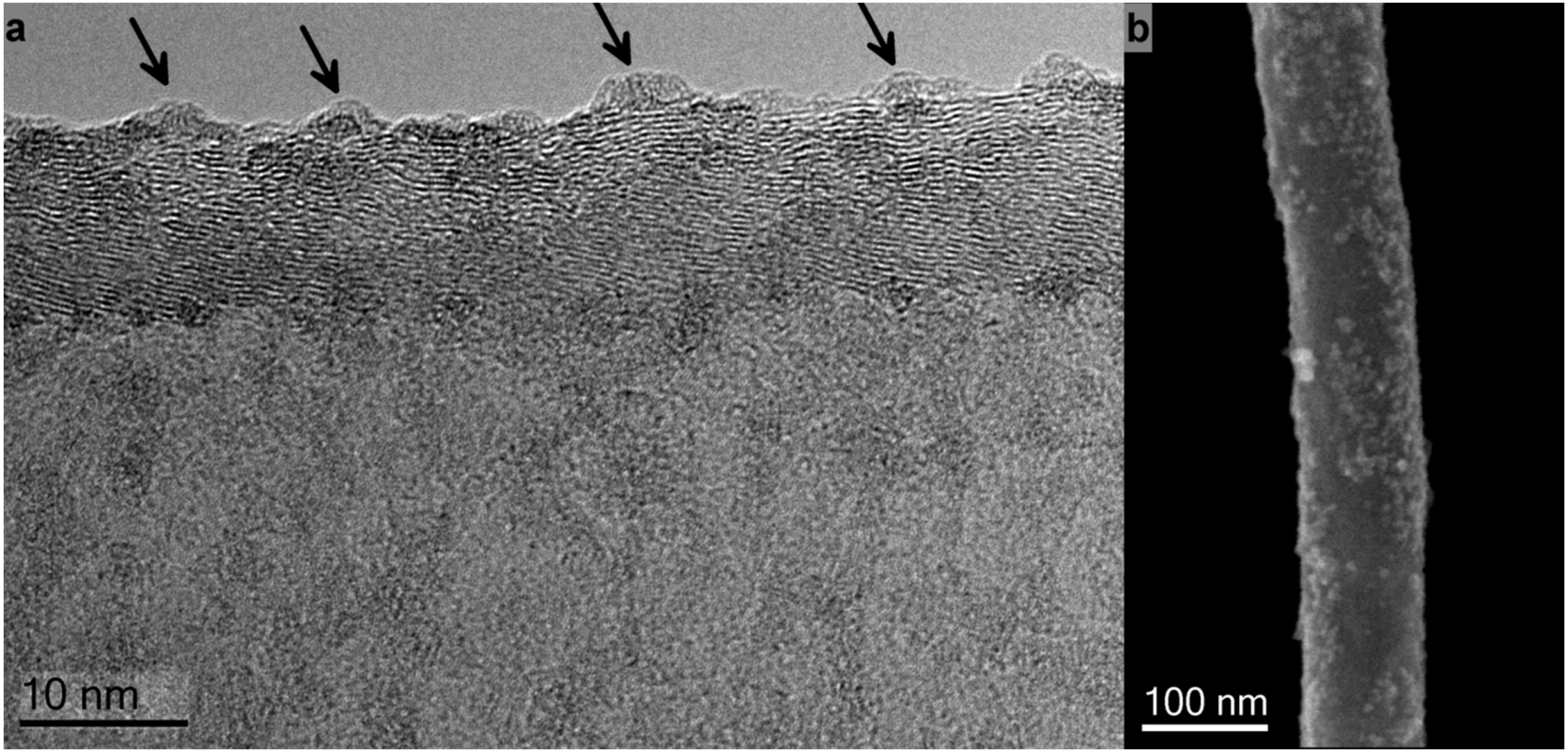
High resolution imaging shows the amorphous character of the as deposited films. However, in the case of V_xO_y films, annealing at 150°C induces crystallization (V_2O_5).

Chemical Analysis

Characterization: Electron Energy Loss Spectrometry (EELS)

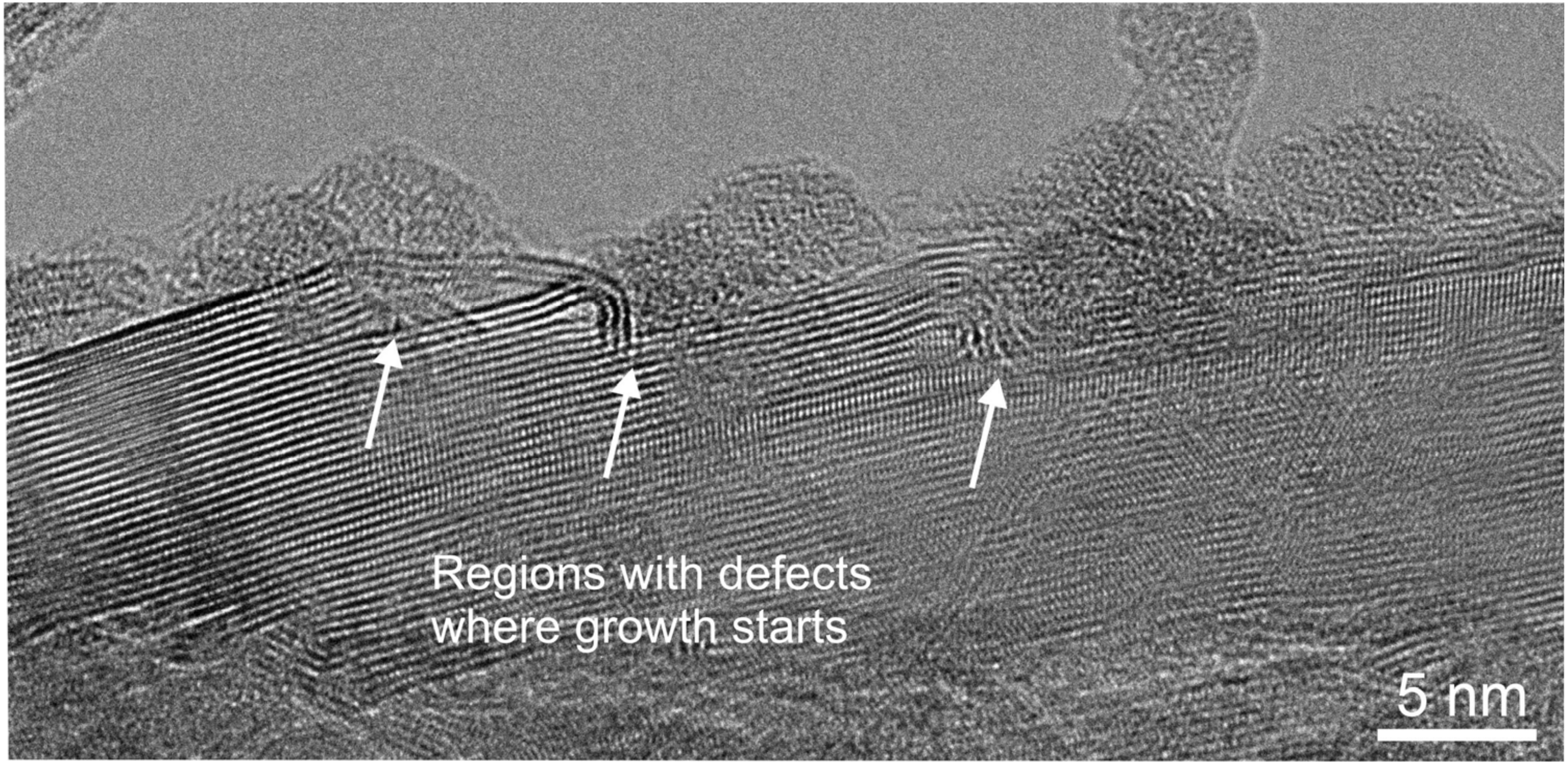


Effect of the CNTs functionalization



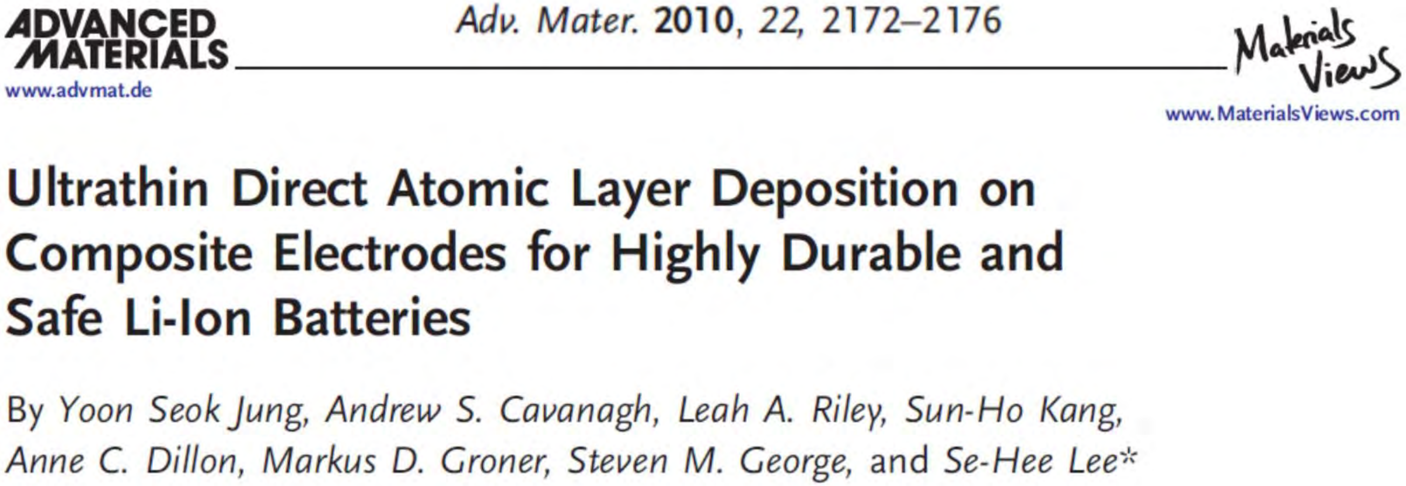
J. Mater. Chem. **2012**, 22, 7323

Effect of the CNTs functionalization



J. Mater. Chem. **2012**, 22, 7323

Applications in Energy Related Fields



ADVANCED MATERIALS
www.advmat.de

Adv. Mater. **2010**, 22, 2172–2176

Materials Views
www.MaterialsViews.com

Ultrathin Direct Atomic Layer Deposition on Composite Electrodes for Highly Durable and Safe Li-Ion Batteries

By *Yoon Seok Jung, Andrew S. Cavanagh, Leah A. Riley, Sun-Ho Kang, Anne C. Dillon, Markus D. Groner, Steven M. George,* and *Se-Hee Lee**

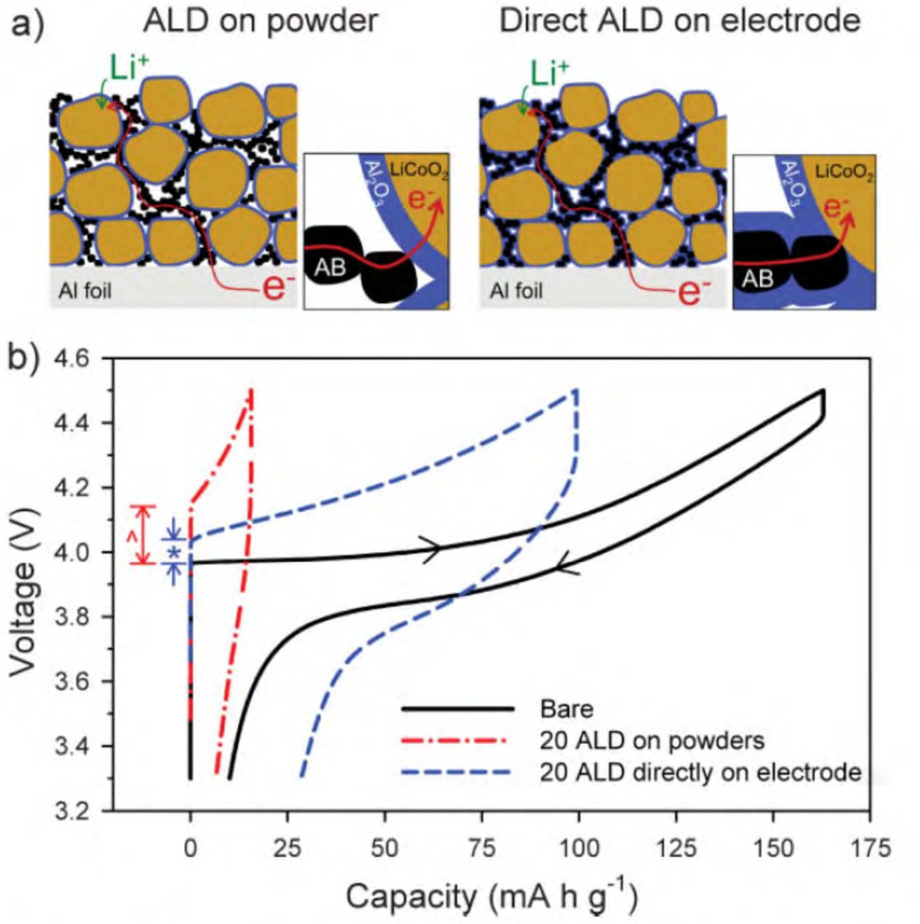
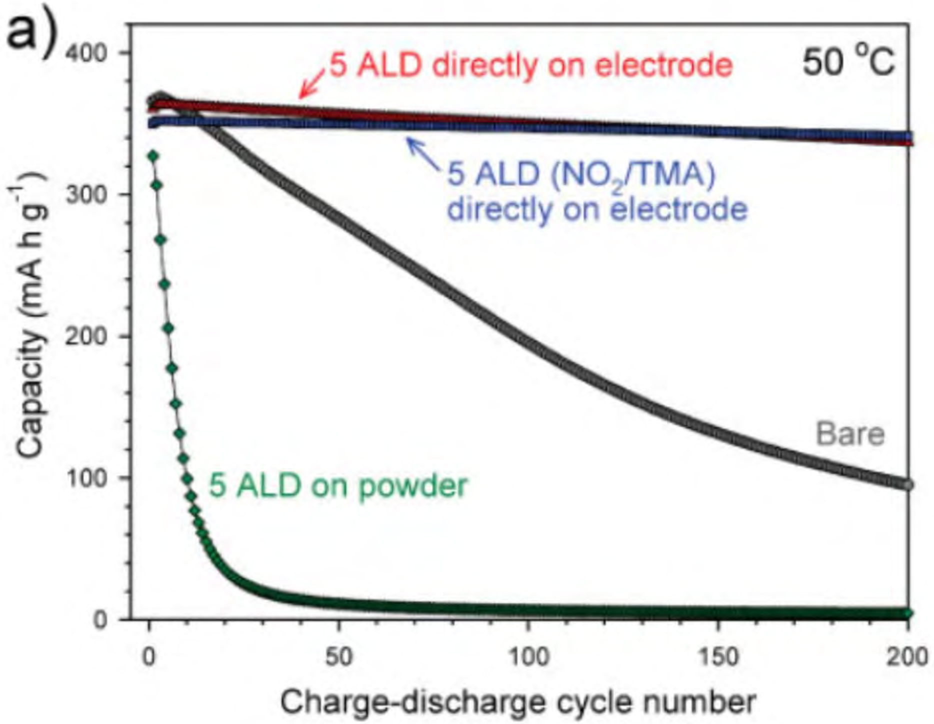


Figure 2. a) Schematics of transport in $LiCoO_2$ composite electrodes when ALD is performed first on the powder versus when ALD is performed directly on the composite electrode. b) Charge–discharge curves at 1 C-rate (140 mA g^{-1}) at room temperature. Note the polarization increase ('∧' and '*') observed for Al_2O_3 coatings with respect to the curve for bare $LiCoO_2$.



Journal of The Electrochemical Society, **157** (1) A75-A81 (2010)
0013-4651/2009/157(1)/A75/7/$28.00 © The Electrochemical Society

Enhanced Stability of $LiCoO_2$ Cathodes in Lithium-Ion Batteries Using Surface Modification by Atomic Layer Deposition

Yoon Seok Jung,[a,*,e] **Andrew S. Cavanagh,**[b] **Anne C. Dillon,**[c,*]
Markus D. Groner,[d] **Steven M. George,**[e] **and Se-Hee Lee**[a,*,z]

[a]*Department of Mechanical Engineering, University of Colorado at Boulder, Boulder, Colorado 80309-0427, USA*
[b]*Department of Physics,* [e]*Department of Chemistry and Biochemistry, and Department of Chemical and Biological Engineering, University of Colorado at Boulder, Boulder, Colorado 80309-0215, USA*
[c]*National Renewable Energy Laboratory, Golden, Colorado 80401, USA*
[d]*ALD NanoSolutions Incorporated, Broomfield, Colorado 80020, USA*

Ultrathin atomic layer deposition (ALD) coatings enhance the performance of lithium-ion batteries (LIBs). Previous studies have demonstrated that $LiCoO_2$ cathode powders coated with metal oxides with thicknesses of ~100 to 1000 Å grown using wet chemical techniques improved LIB performance. In this study, $LiCoO_2$ powders were coated with conformal Al_2O_3 ALD films with thicknesses of only ~3 to 4 Å established using two ALD cycles. The coated $LiCoO_2$ powders exhibited a capacity retention of 89% after 120 charge–discharge cycles in the 3.3–4.5 V (vs Li/Li^+) range. In contrast, the bare $LiCoO_2$ powders displayed only a 45% capacity retention. Al_2O_3 ALD films coated directly on the composite electrode also produced improved capacity retention. This dramatic improvement may result from the ultrathin Al_2O_3 ALD film acting to minimize Co dissolution or reduce surface electrolyte reactions. Similar experiments with ultrathin ZnO ALD films did not display enhanced performance.
[DOI: 10.1149/1.3258274]

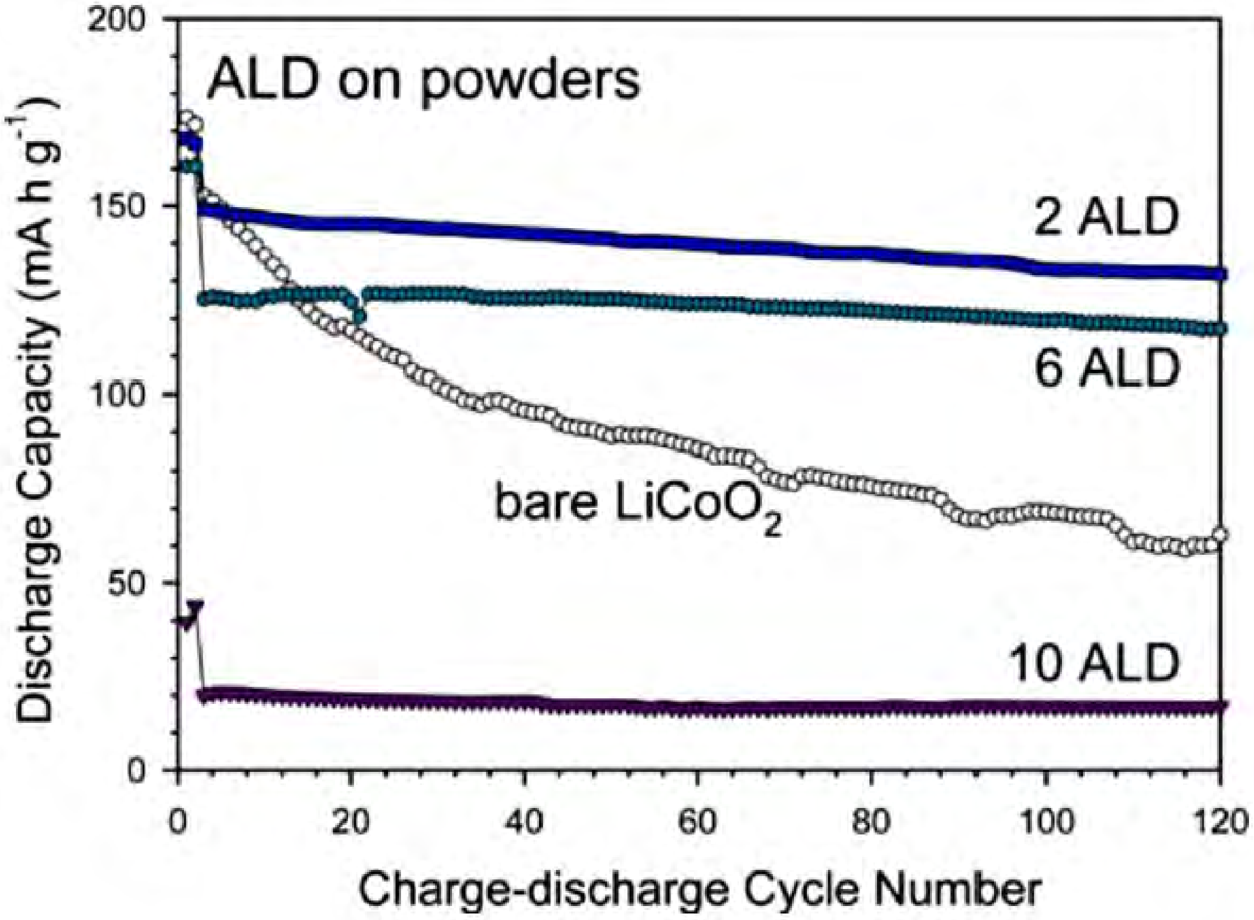


Figure 8. (Color online) Charge–discharge cycle performance of electrodes fabricated using the bare $LiCoO_2$ powders and the Al_2O_3 ALD-coated $LiCoO_2$ powders using 2, 6, and 10 ALD cycles.

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Vol. 7, No. 8
2183−2187

ZnO Nanotube Based Dye-Sensitized Solar Cells

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Received January 20, 2007; Revised Manuscript Received May 25, 2007

ABSTRACT

We introduce high surface area ZnO nanotube photoanodes templated by anodic aluminum oxide for use in dye-sensitized solar cells (DSSCs). Atomic layer deposition is utilized to coat pores conformally, providing a direct path for charge collection over tens of micrometers thickness. Compared to similar ZnO-based devices, ZnO nanotube cells show exceptional photovoltage and fill factors, in addition to power efficiencies up to 1.6%. The novel fabrication technique provides a facile, metal-oxide general route to well-defined DSSC photoanodes.

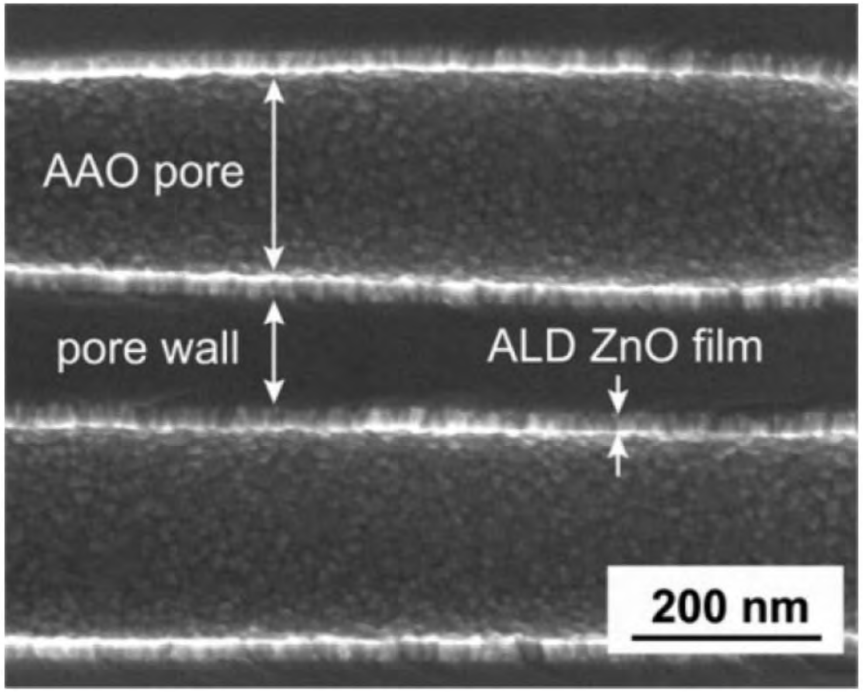


Figure 1. Cross-sectional SEM image of commercial AAO membrane pores coated with 20 nm of ZnO by ALD.

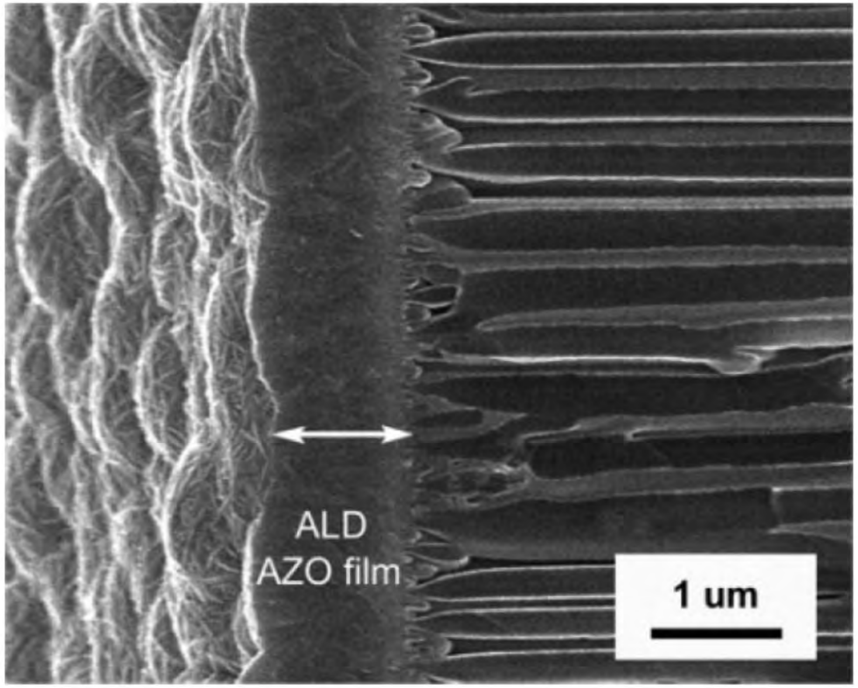
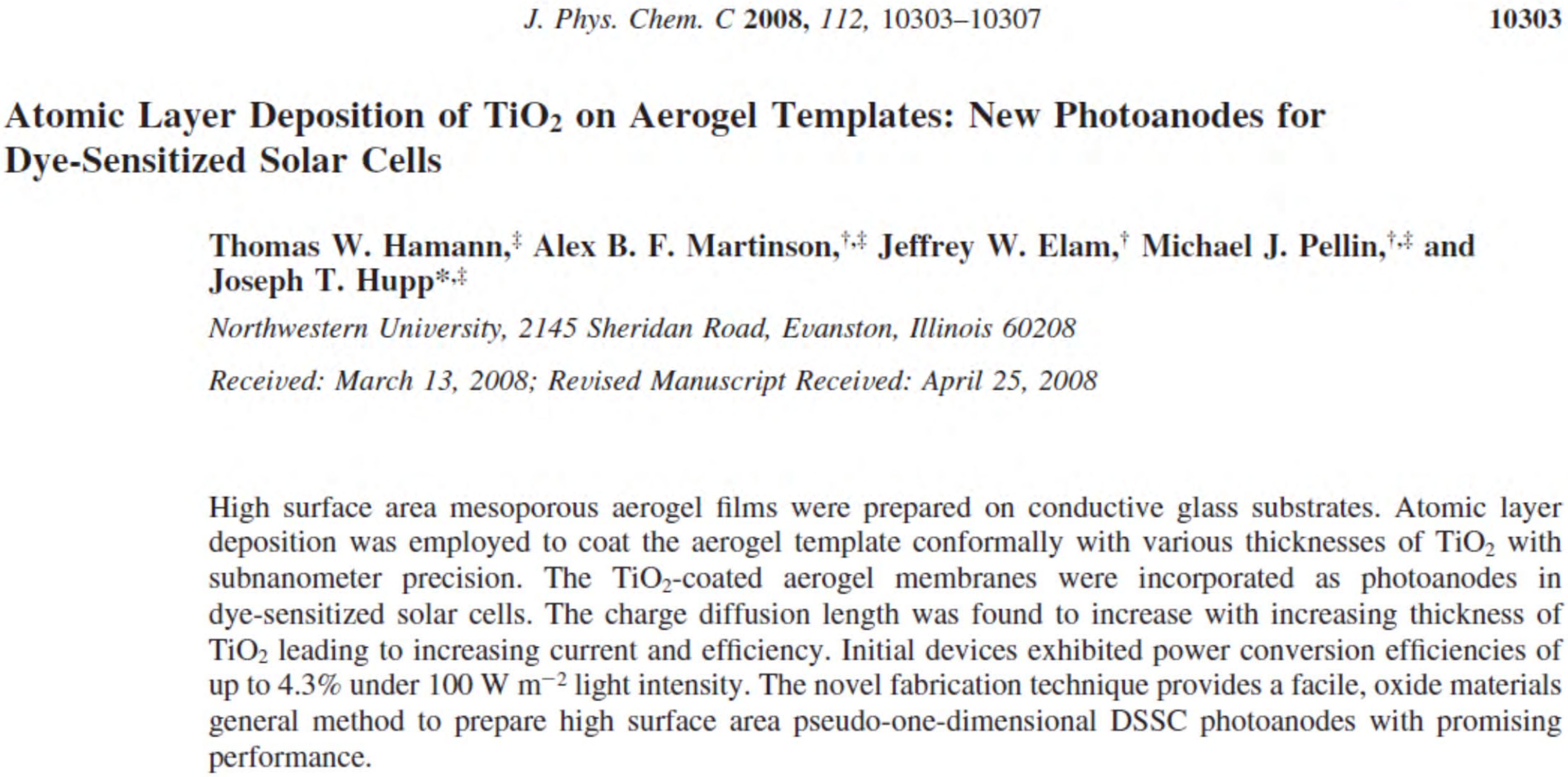


Figure 2. Cross-sectional SEM image of commercial AAO face coated with transparent conductive oxide AZO.



J. Phys. Chem. C **2008,** *112,* 10303–10307 **10303**

Atomic Layer Deposition of TiO_2 on Aerogel Templates: New Photoanodes for Dye-Sensitized Solar Cells

Thomas W. Hamann,[‡] Alex B. F. Martinson,[†,‡] Jeffrey W. Elam,[†] Michael J. Pellin,[†,‡] and Joseph T. Hupp*[,‡]

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Received: March 13, 2008; Revised Manuscript Received: April 25, 2008

High surface area mesoporous aerogel films were prepared on conductive glass substrates. Atomic layer deposition was employed to coat the aerogel template conformally with various thicknesses of TiO_2 with subnanometer precision. The TiO_2-coated aerogel membranes were incorporated as photoanodes in dye-sensitized solar cells. The charge diffusion length was found to increase with increasing thickness of TiO_2 leading to increasing current and efficiency. Initial devices exhibited power conversion efficiencies of up to 4.3% under 100 W m^{-2} light intensity. The novel fabrication technique provides a facile, oxide materials general method to prepare high surface area pseudo-one-dimensional DSSC photoanodes with promising performance.

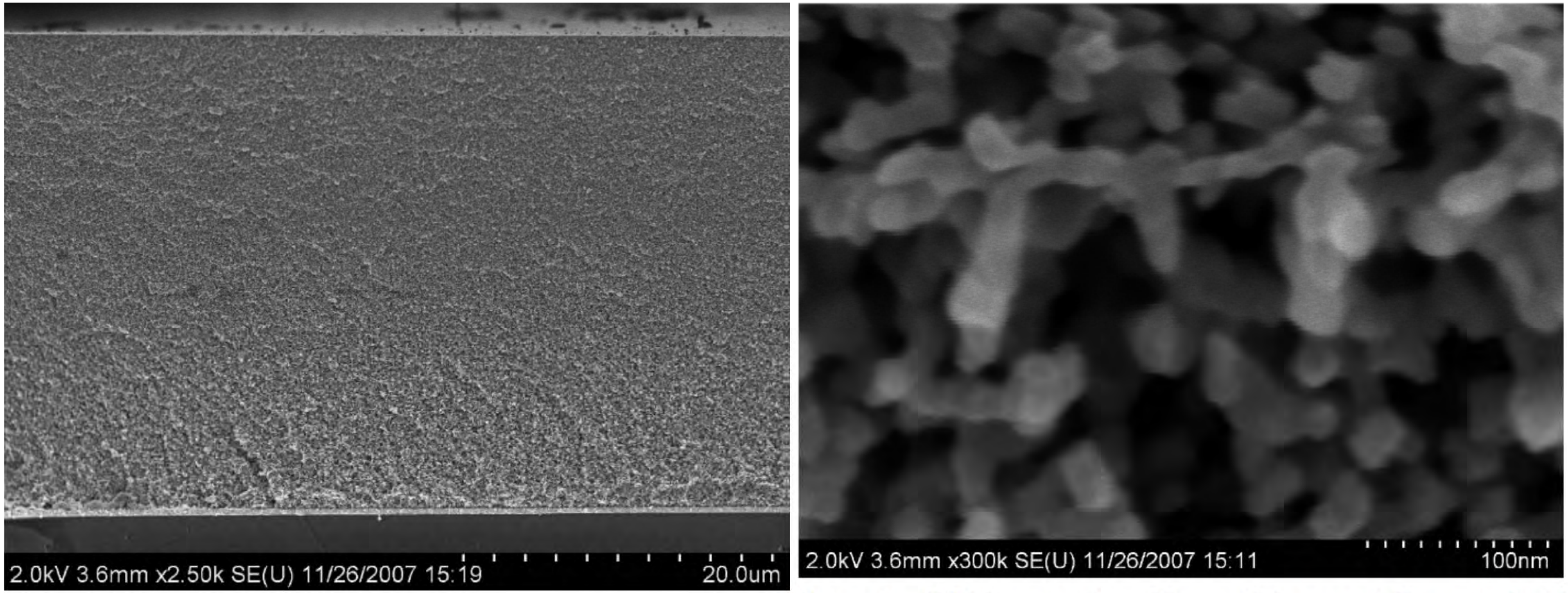
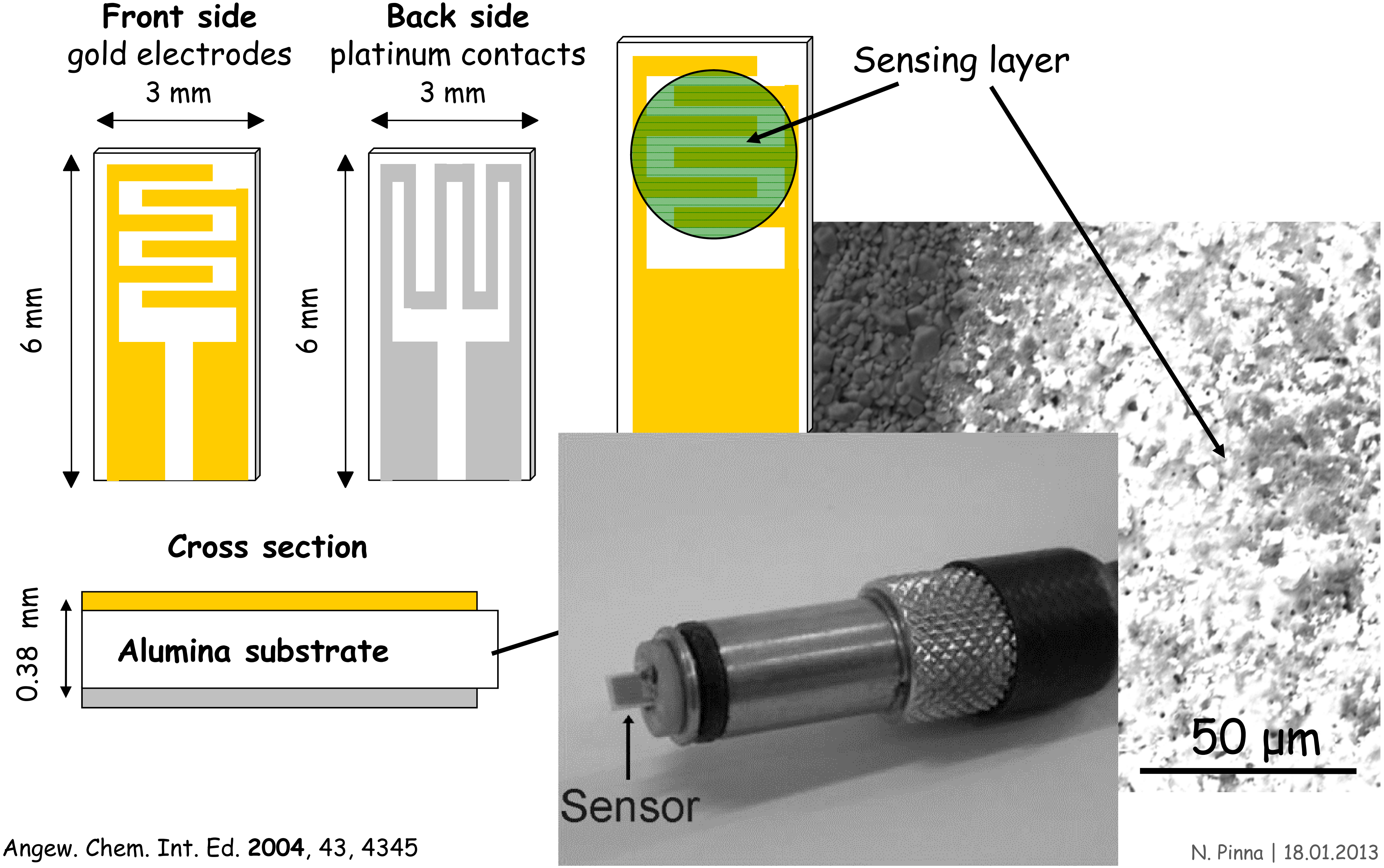


Figure 1. SEM images of a $\sim$30 μm thick aerogel film coated with 9.6 nm TiO_2.

Gas Sensors



Front side
gold electrodes
3 mm
6 mm

Back side
platinum contacts
3 mm
6 mm

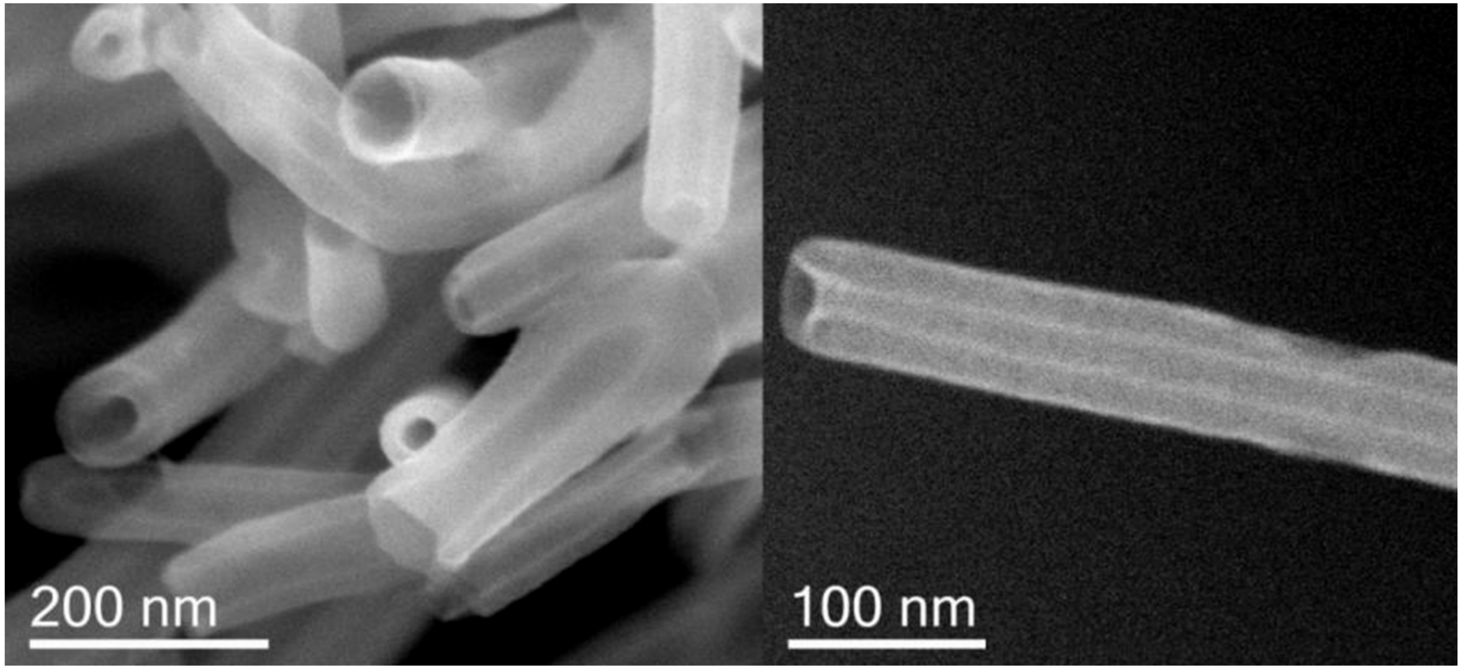
Sensing layer

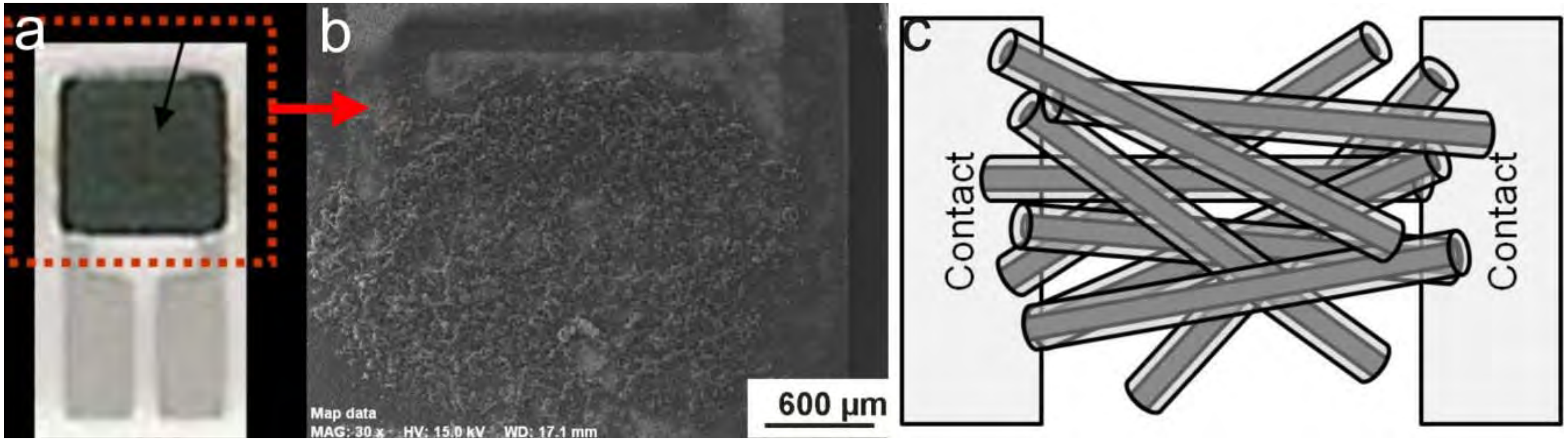
50 µm

Cross section
0.38 mm
Alumina substrate

Sensor

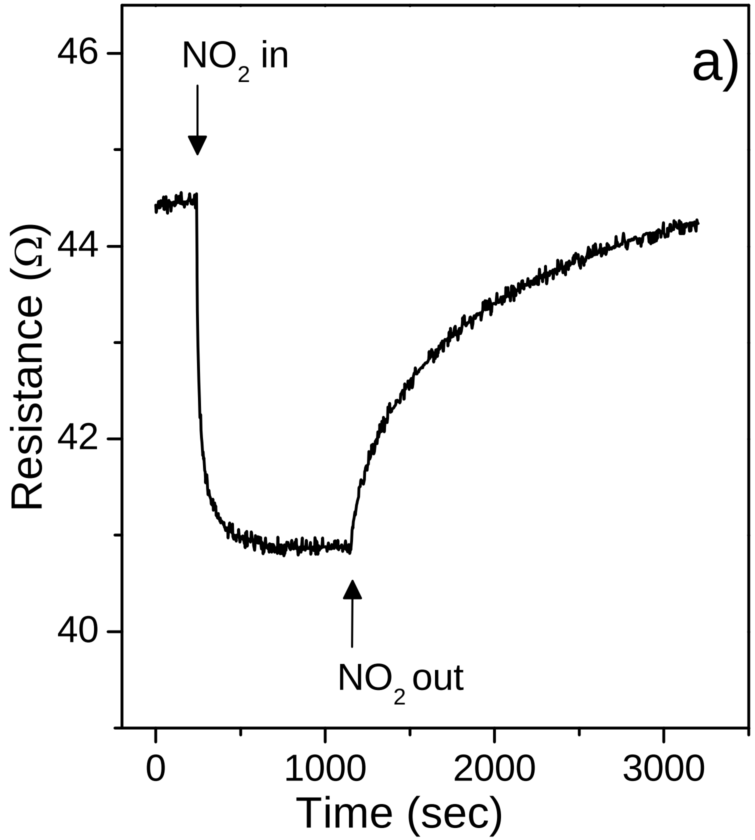
Angew. Chem. Int. Ed. **2004**, 43, 4345



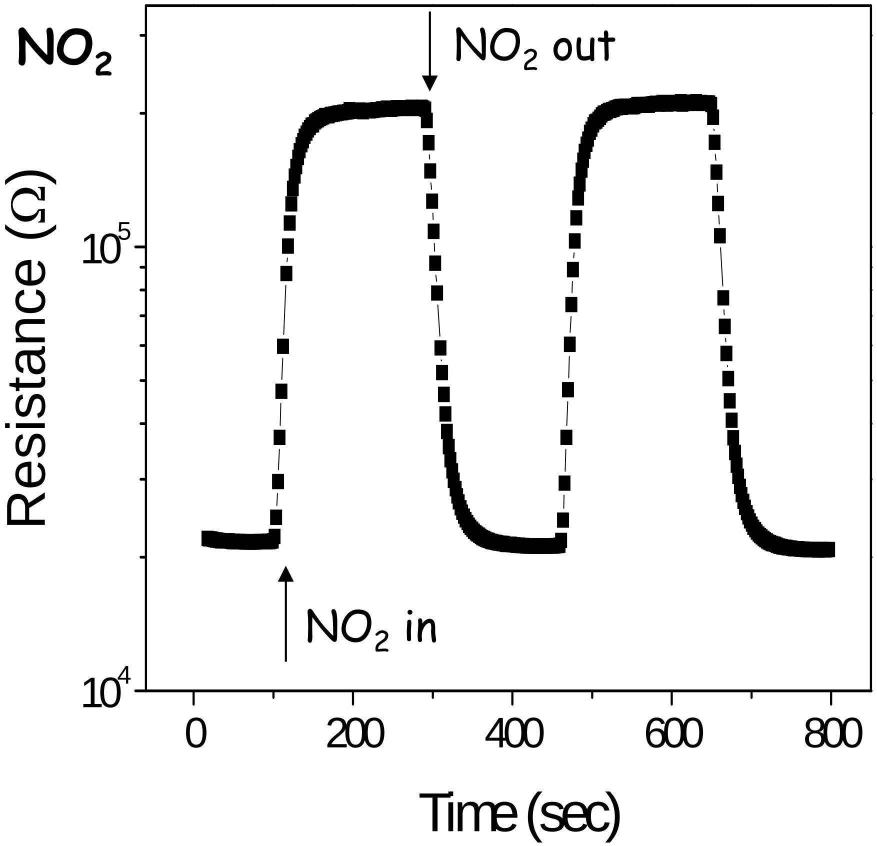


Nano Lett. **2008**, 8, 4201 - Phys. Chem. Chem. Phys. **2009**, 11, 3615 - Adv. Funct. Mater. **2011**, 21, 658

SnO_2 coated CNTs



5 ppm NO_2

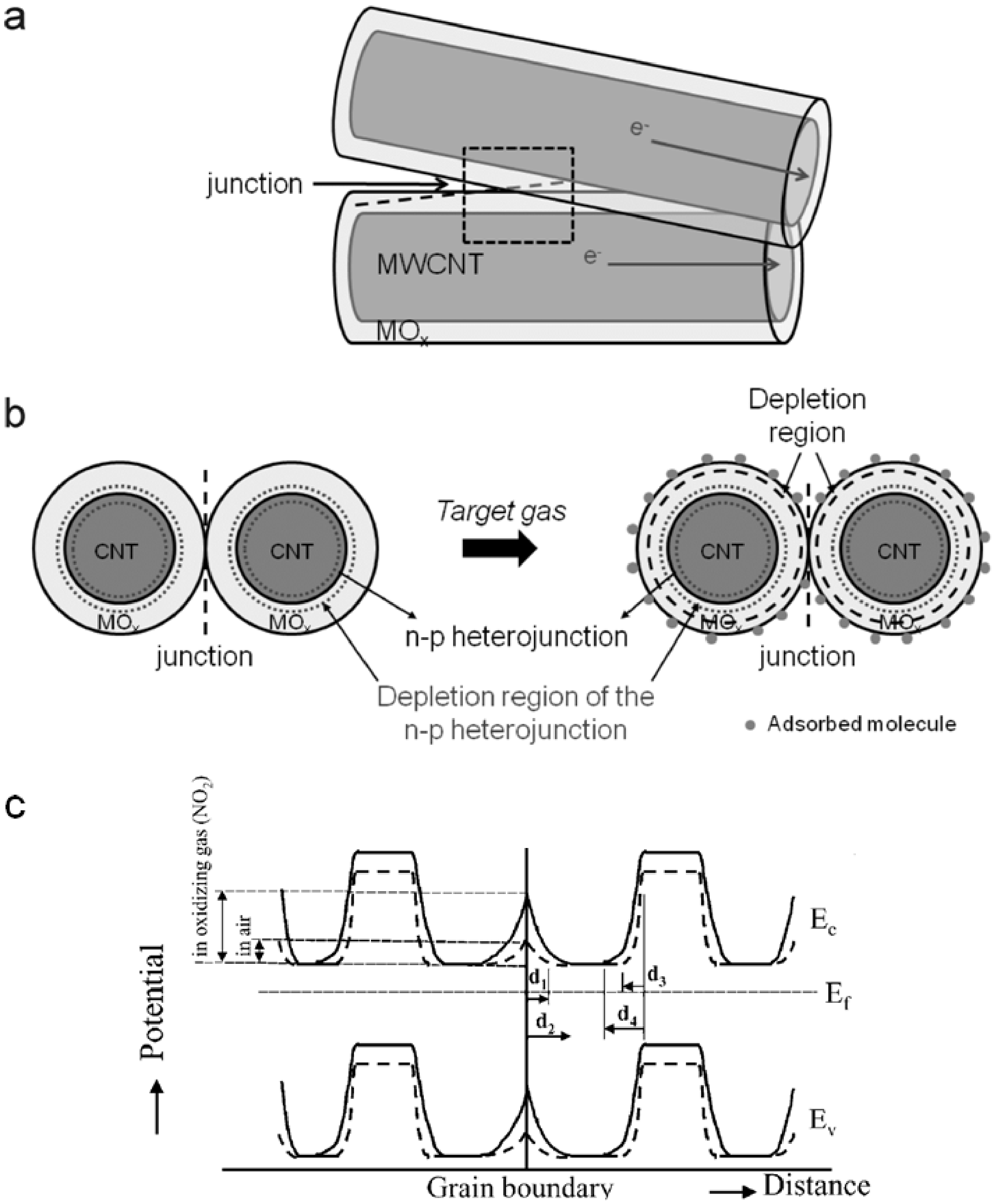


Pure CNTs are p-type semi-conductors

SnO_2 coated CNTs are n-type semiconductors

→ formation of a p-n heterojunction between the metal oxide film and support

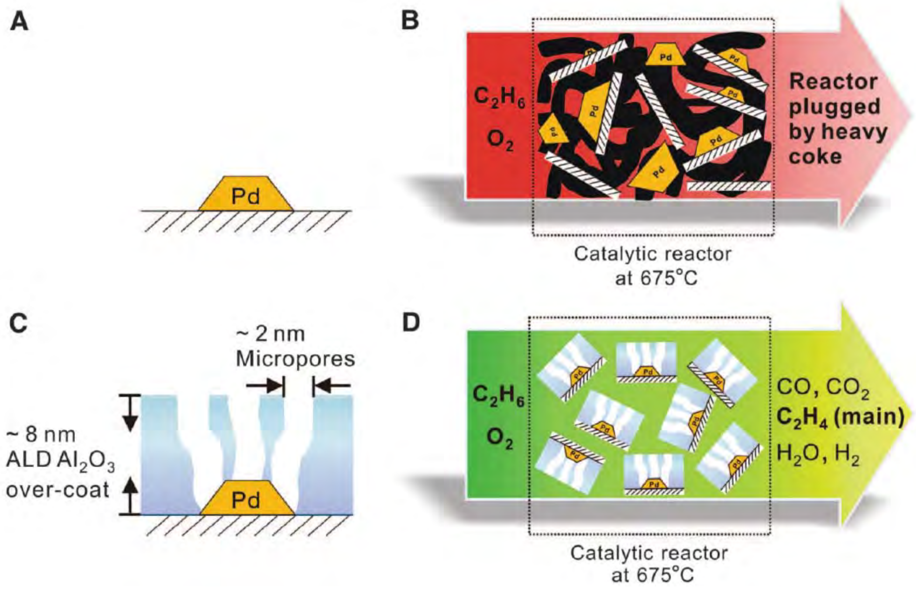
Nano Lett. **2008**, 8, 4201 - Adv. Funct. Mater. **2011**, 21, 658

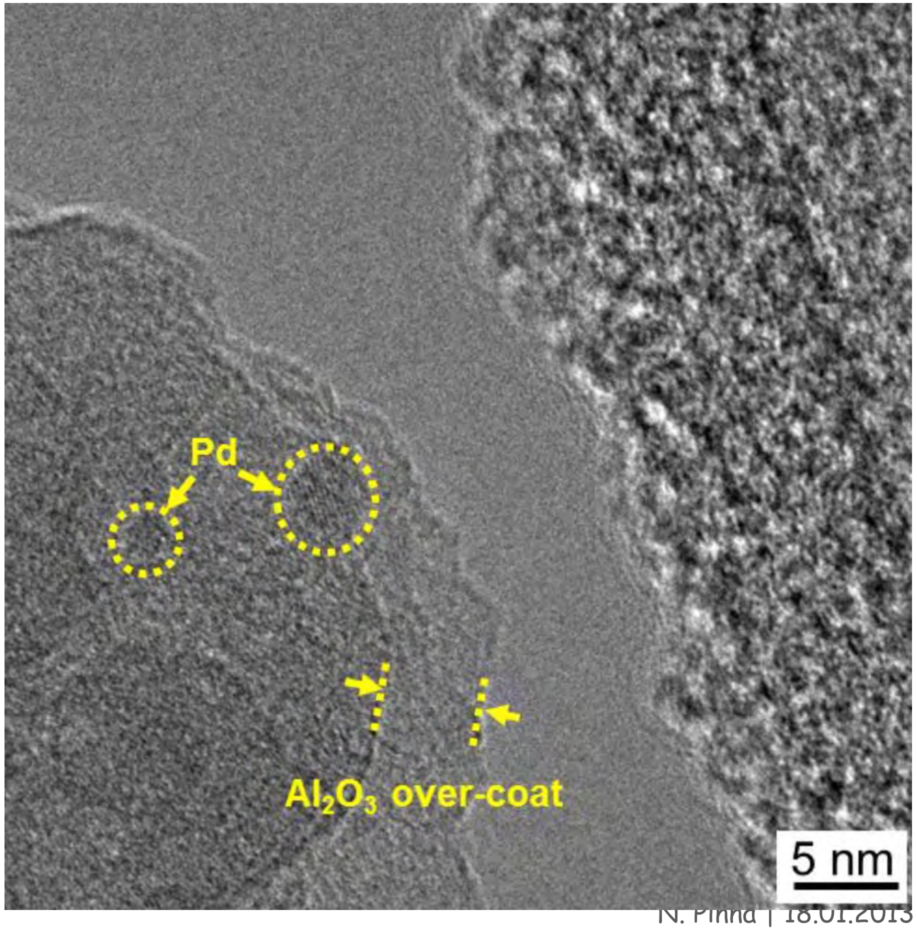

a
junction
e-
e-
MWCNT
MO_x
b
Depletion region
CNT
CNT
MO_x
MO_x
junction
Target gas
n-p heterojunction
CNT
CNT
MO_x
MO_x
junction
Depletion region of the n-p heterojunction
● Adsorbed molecule
c
in oxidizing gas (NO_2)
in air
Potential
E_c
E_f
E_v
d_1
d_2
d_3
d_4
Grain boundary
Distance

Coking- and Sintering-Resistant Palladium Catalysts Achieved Through Atomic Layer Deposition

Junling Lu,[1] Baosong Fu,[2] Mayfair C. Kung,[3] Guomin Xiao,[2] Jeffrey W. Elam,[1]
Harold H. Kung,[3] Peter C. Stair[4,5]*

Oxidative dehydrogenation of ethane to ethylene at 650 °C





SCIENCE, 2012, 335,1205

Shape-selective sieving layers on an oxide catalyst surface

Christian P. Canlas[1], Junling Lu[2], Natalie A. Ray[3], Nicolas A. Grosso-Giordano[4], Sungsik Lee[5], Jeffrey W. Elam[2], Randall E. Winans[5], Richard P. Van Duyne[1,3], Peter C. Stair[1,3,6] and Justin M. Notestein[1,4]*

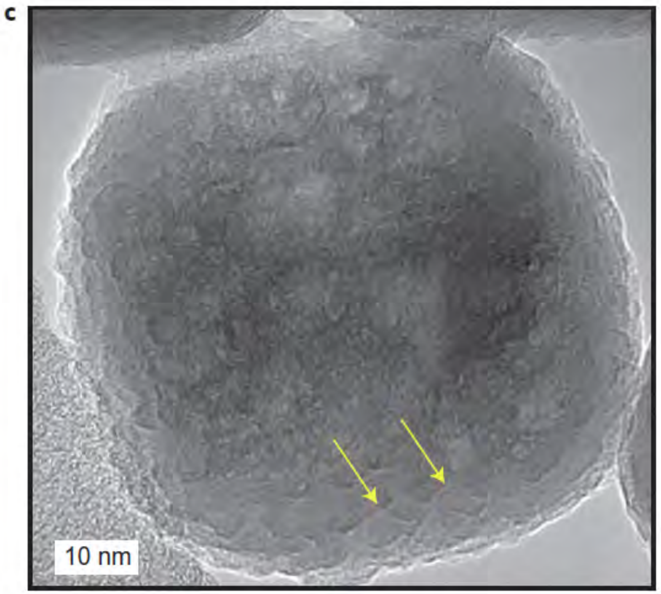


Figure 3 | TEM images show ALD-coated $SrTiO_3$ nanocuboids. **a**, Ten cycles of ALD Al_2O_3 on $SrTiO_3$ nanocuboids gives relatively smooth surfaces. **b**, High-magnification image of the roughened interface for 10 cycles of ALD Al_2O_3 on CAL-$SrTiO_3$, showing the atomically flat surface of the underlying crystal. **c**, Low-magnification image after 10 cycles of ALD Al_2O_3 on CAL-$SrTiO_3$ nanocuboids shows a much roughened surface compared to **a**. Arrows highlight several candidate nanocavities. (See Supplementary Fig. S4 for additional images and magnifications.)

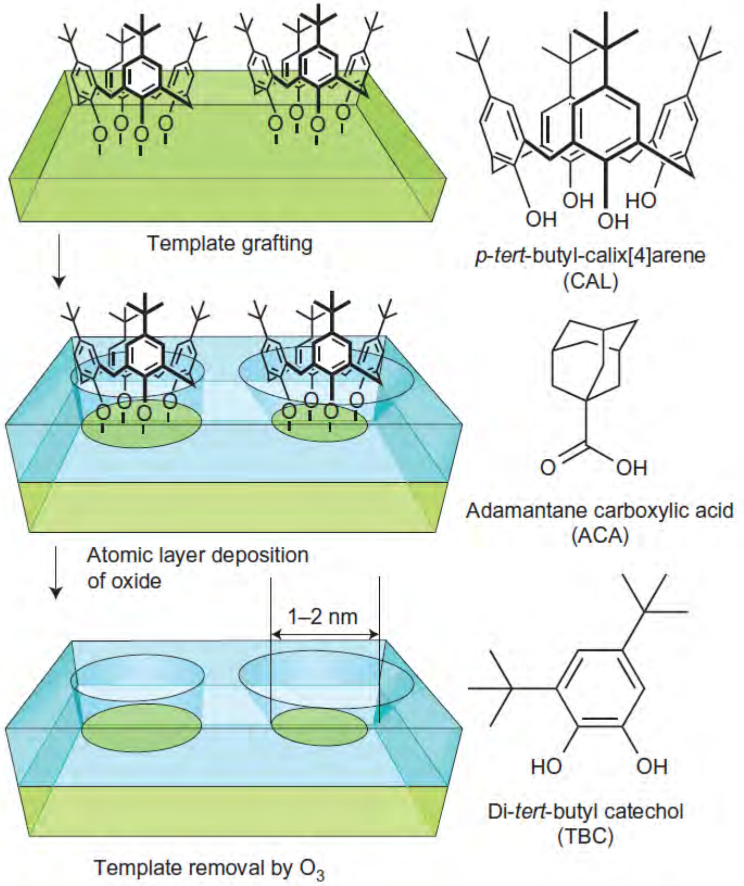


Figure 1 | Nanocavity oxides selectively allow access only to molecules able to penetrate the <2-nm-diameter supermicroporous cavities. They are synthesized by (i) depositing a template (right) onto an existing catalyst surface, (ii) using ALD to synthesize an inert oxide film <2 nm thick around, but not over, the templates, and (iii) treating the materials in O_3 to remove the templates, revealing the underlying catalyst surface.

NATURE CHEMISTRY, 2012, 4, 1031