

Nanášanie po atómových vrstvách: prvé experimentálne výsledky

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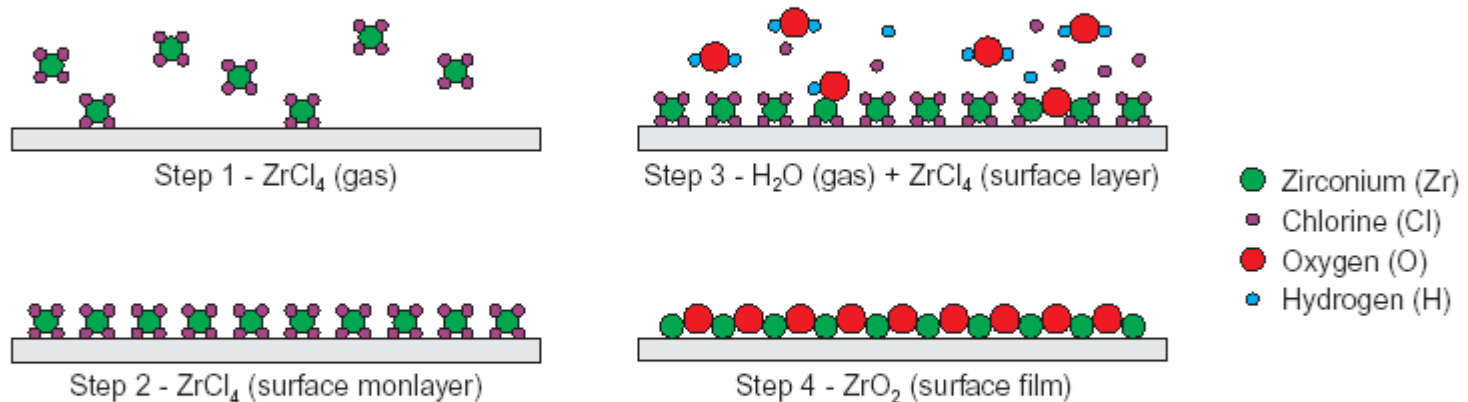
Projekt štrukturálnych fondov EÚ

Budovanie Centra excelentnosti pre nové technológie v elektrotechnike – II. etapa

Aktivita 2.2 Zvýšenie výskumného potenciálu Centra v príprave tenkých vrstiev nanášaním po atómových vrstvách

- Výber a obstaranie zariadenia ALD: september 2011
- Uvedenie zariadenia ALD do prevádzky. október 2011
- Príprava experimentálnych štruktúr a súčiastok. október 2011 – február 2013

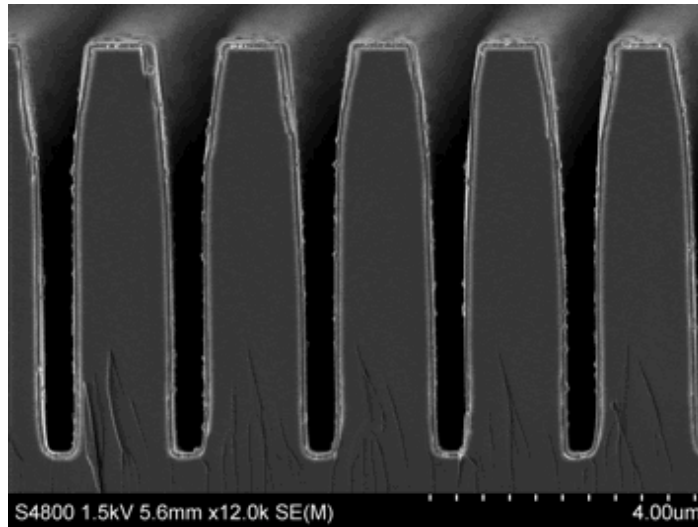
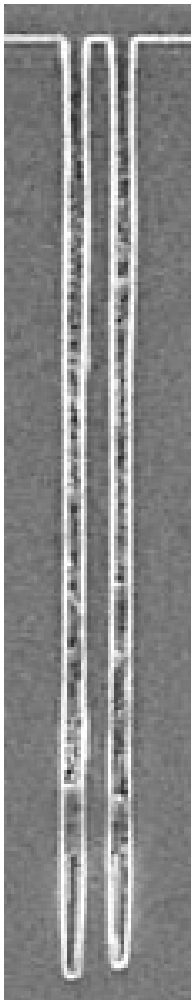
Atomic Layer Deposition (ALD)



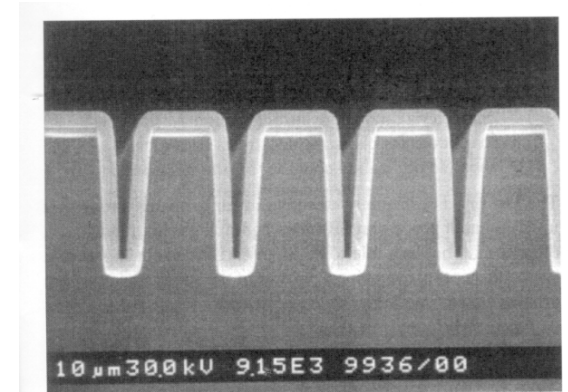
Atomic Layer Deposition (ALD) utilizes sequential precursor gas pulses to deposit a film one layer at a time. As illustrated in the figure above, the first precursor gas is introduced into the process chamber and produces a monolayer of gas on the wafer surface. A second precursor of gas is then introduced into the chamber reacting with the first precursor to produce a monolayer of film on the wafer surface. Since each pair of gas pulses (one cycle) produces exactly one monolayer of film the thickness of the resulting film may be precisely controlled by the number of deposition cycles.

Atomic layer deposition: DRAM capacitors

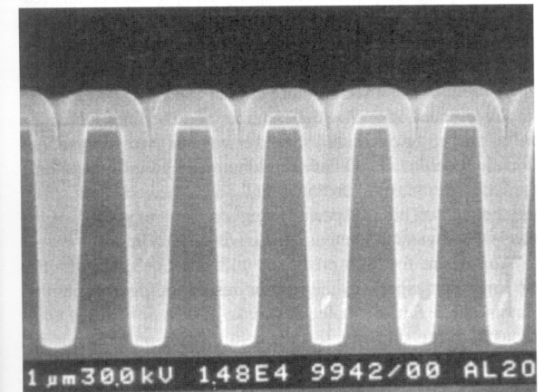
Cross-sectional SEM of a HfO_2 coating inside a hole with an aspect ratio of 35:1. Capacitors for DRAM memory elements.



Conformal coating in deep trenches. Capacitors for DRAM memory elements.



(a)



(b)

Fig. 2. Cross-sectional SEM images of a 300-nm Al_2O_3 film deposited onto a patterned silicon substrate showing (a) perfect conformality and (b) trench-fill capability [88]. Note that on the top surface of the silicon wafer there is a thermal silicon oxide layer below the Al_2O_3 film. Reprinted with permission from M. Ritala et al., Perfectly conformal TiN and Al_2O_3 films deposited by atomic layer deposition, *Chem. Vapor Deposition* 5, 7 (1999), © 1999, Wiley-VCH Verlag GmbH.

Atomic layer deposition at IEE SAS



Beneq TFS 200

- thermal, plasma assisted ALD
 - up to 200 mm wafers
- liquid source: Al₂O₃ (TMA), H₂O
 - hot source 300: (TiO₂, HfO₂, ZrO₂)
 - hot source 500
 - load-lock
- deposition up 400 °C
 - O₃ option

First experiments

Deposition of Al₂O₃ at 200 °C using thermal ALD

Precursor: TMA, Al (CH₃)₃

Substrates: Si + native SiO₂, Si + 100 nm thermal SiO₂, 2 nm HfO₂

ALD of Al₂O₃ thin films - Experimental

Precursor: Trimethylaluminium (Al(CH₃)₃)

Reactant: H₂O vapours thermal ALD
Ar/O plasma plasma enhanced ALD

Purging gas: N₂

Deposition temperature: 100, 200 °C

Characterization:

X-ray reflectivity (AXS-D8 Discovery, Bruker)

Ellipsometry (J. A. Woollam)

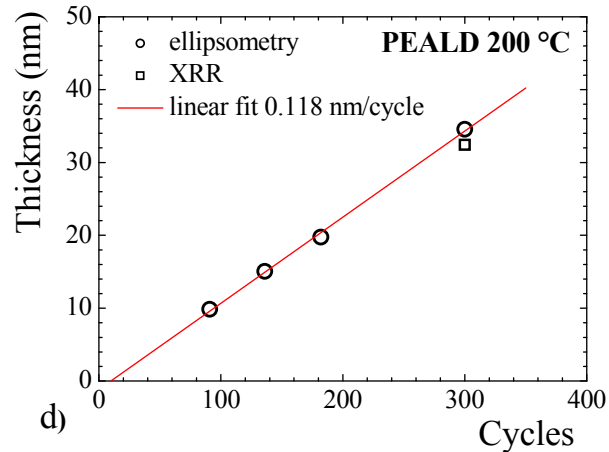
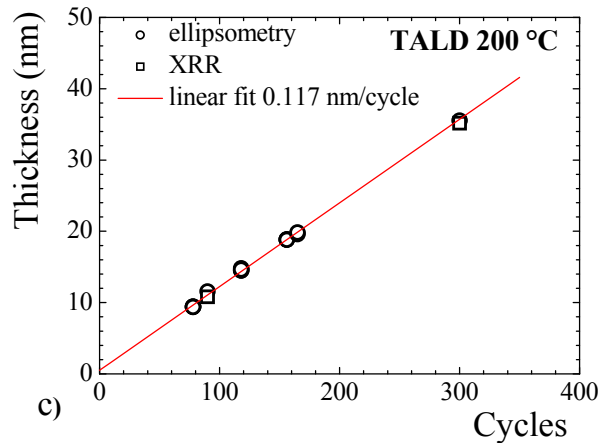
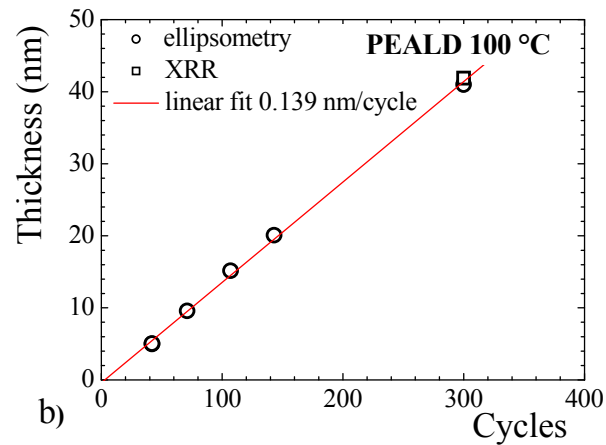
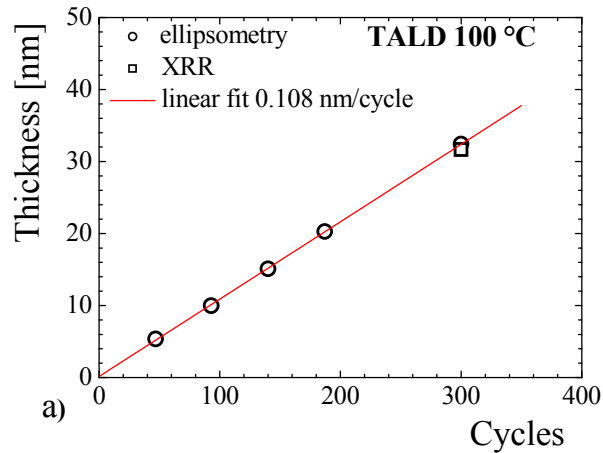
X-ray photoelectron spectroscopy (Thermo Fisher Scientific)

ALD of Al₂O₃ thin films - Experimental

ALD Process	Temperature [°C]	Pulsing times [s]
		Precursor dosing/purging/reactant exposure/purging
Thermal	100	0.25 / 10 / 0.25 / 20
Plasma enhanced	100	0.25 / 10 / 3 / 20
Thermal	200	0.25 / 5 / 0.25 / 10
Plasma enhanced	200	0.25 / 5 / 3 / 10

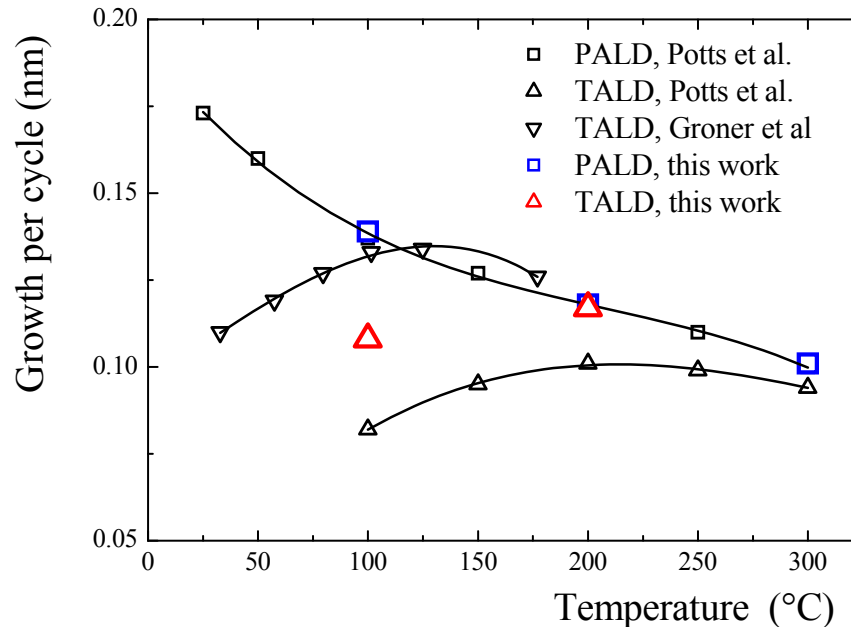
Determination of pulsing times to achieve self-limiting character of the process

ALD of Al₂O₃ thin films – determination of GPC



Thickness Al₂O₃ film as a function of ALD cycles for a) thermal ALD at 100 °C, b) plasma enhanced ALD at 100 °C, c) thermal ALD at 200 °C and d) plasma enhanced ALD at 200 °C.

ALD: Properties of Al₂O₃ thin films - Results



Monolayer for Al₂O₃ \cong 0.38 nm

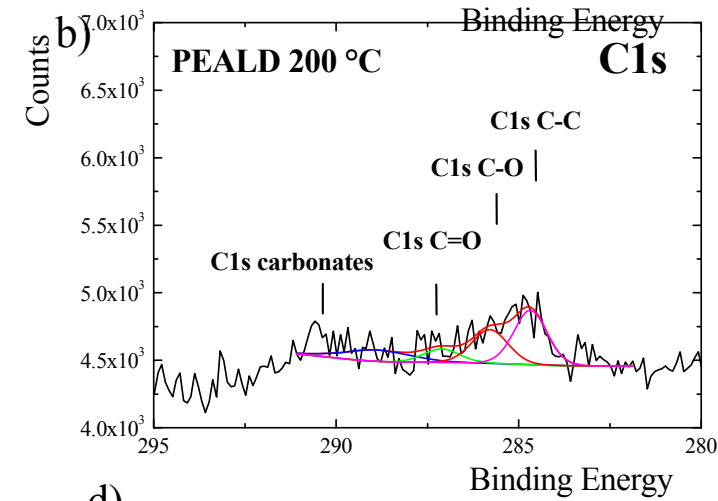
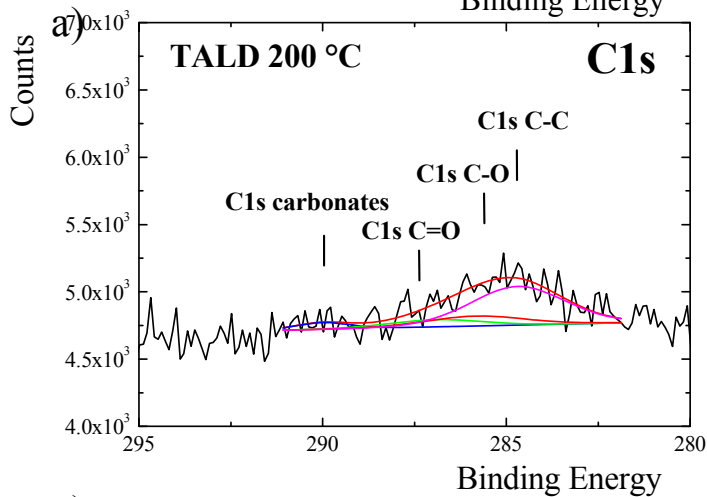
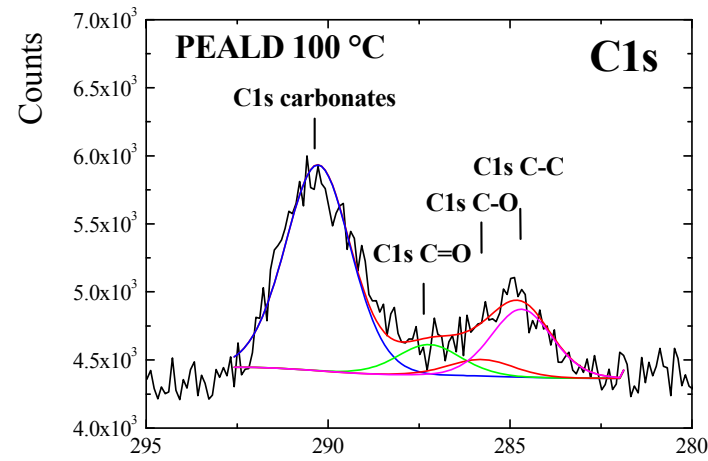
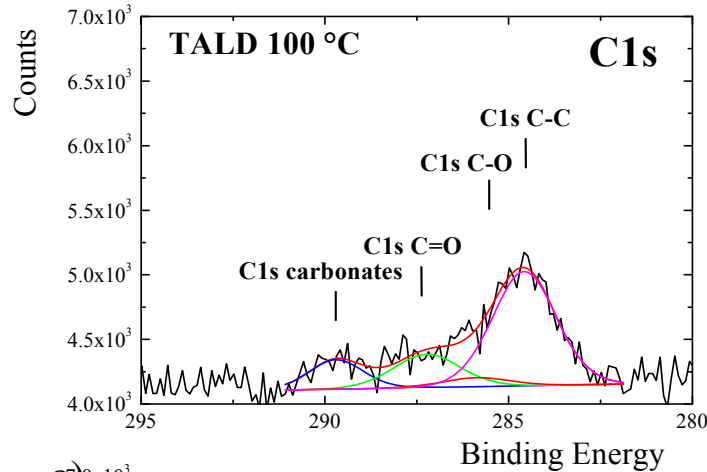
S. E. Potts et al. J. Electrochem. Soc. 157 (2010) P66.

M. D. Groner et al. Chem. Mater. 16 (2004) 639.

TALD: GPC decreases with temperature lowering due to insufficient thermal energy for reaction of H₂O with the surface - hydroxyl states density (-OH) decreases.

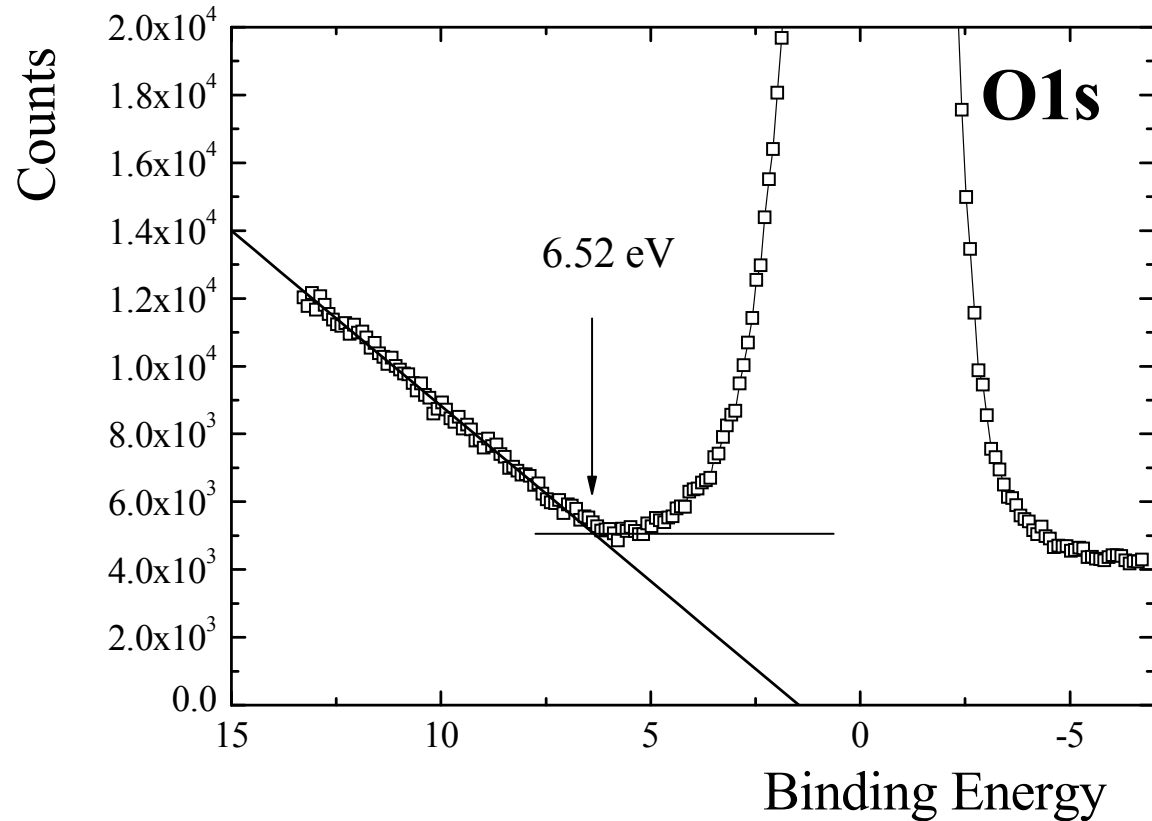
PEALD: GPC increases with temperature lowering due higher surface density of hydroxyl groups at lower temperature due to plasma excitation.

ALD of Al₂O₃ thin films – Carbon content



C1s spectra for the Al₂O₃ films prepared by) thermal ALD at 100 °C, b) plasma enhanced ALD at 100 °C, c) thermal ALD at 200 °C and d) plasma enhanced ALD at 200 °C.

ALD of Al₂O₃ thin films – Band gap determination



Determination of the band gap from the onset of the energy-loss spectra of O1s photoelectrons

S. Miyazaki, J. VaC. Sci. Technol. B **19** (2001) 2212.

ALD: Properties of Al₂O₃ thin films - Summary

Summary of properties of the Al₂O₃ films.

Sample	Thickness [nm]	Process	GPC [nm]	O/Al	C [at %]	E _g [eV]
A-Al-77	32.4	thermal ALD 100 °C	0.108	1,42	0,9	6.17
A-Al-78	41.0	plasma enhanced ALD 100 °C	0.139	1,48	1,9	6.42
A-Al-80	35.5	thermal ALD 200 °C	0.117	1,37	0,2	6.52
A-Al-79	34.6	plasma enhanced ALD 200 °C	0.118	1,37	0,1	6.70

O/Al ratio: Nearly stoichiometric Al₂O₃ using PEALD at 100 °C. Slightly substoichiometric Al₂O₃ at 200 °C.

Carbon impurity: increased content of carbon impurities for the films deposited at 100 °C.

Band gap: ranges from 6.17 eV for TALD, 100 °C to 6.70 eV for PEALD, 200 °C.

Vd'aka za pozornost'