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Synthesis of complex oxides by ALCVD

Ola Nilsen

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CVD

Chemical Vapour Deposition

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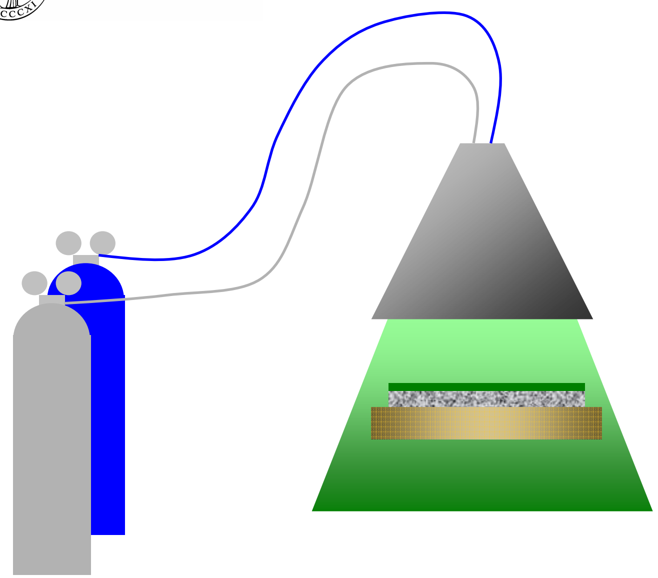
CVD (Chemical Vapour Deposition)



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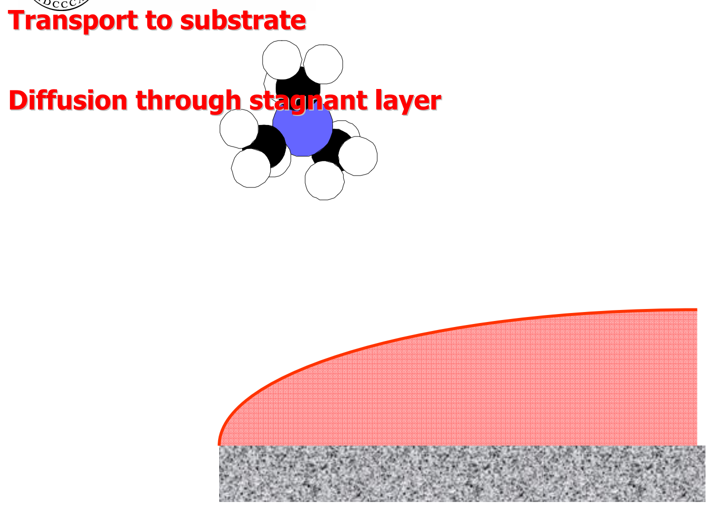
CVD kinetics



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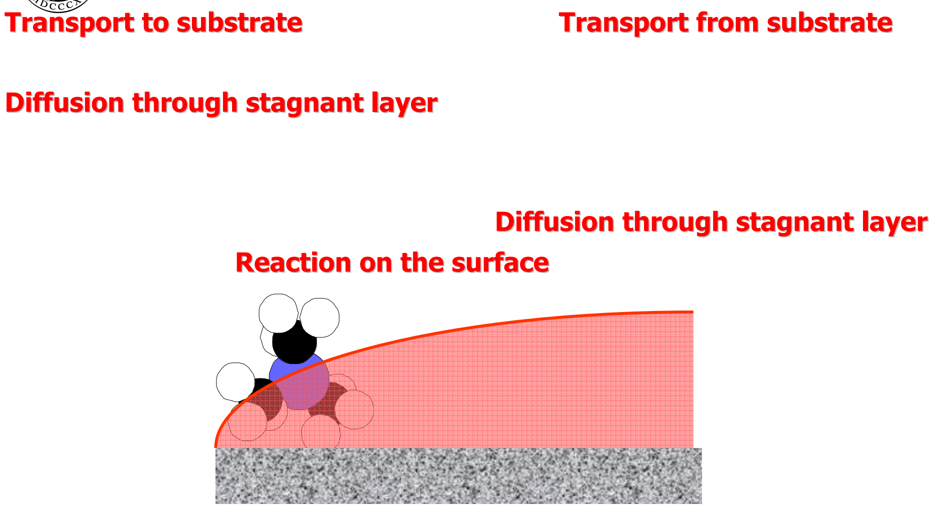
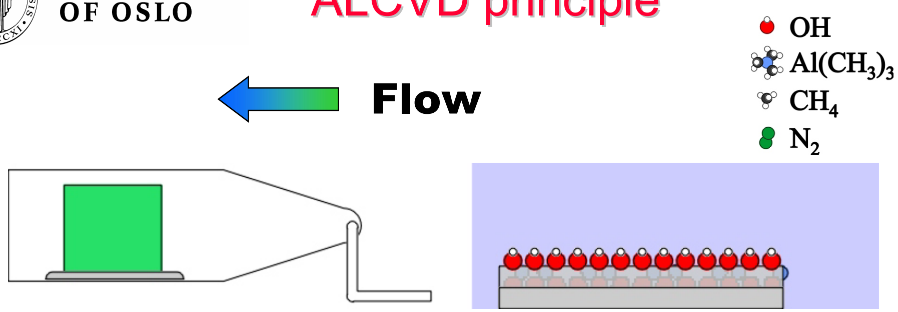
CVD kinetics

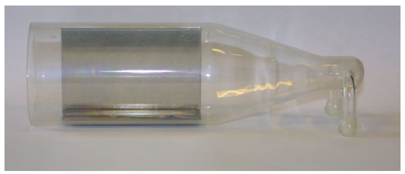


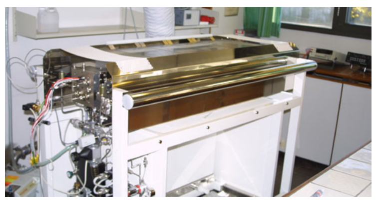
ALCVD

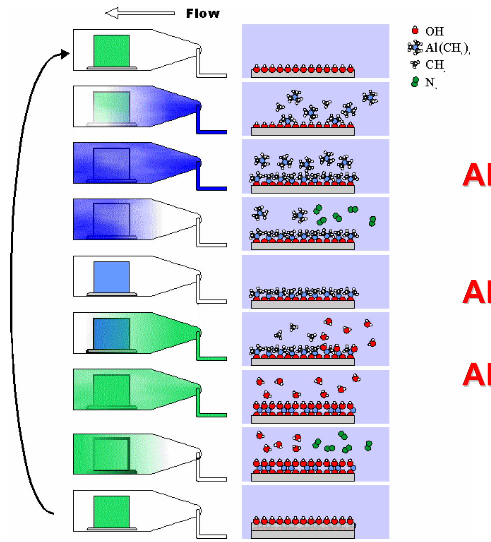
Atomic Layer Chemical Vapour Deposition

ALCVD principle









ALCVD Atomic Layer Chemical Vapour Deposition

ALD Atomic Layer Deposition

ALE Atomic Layer Epitaxy

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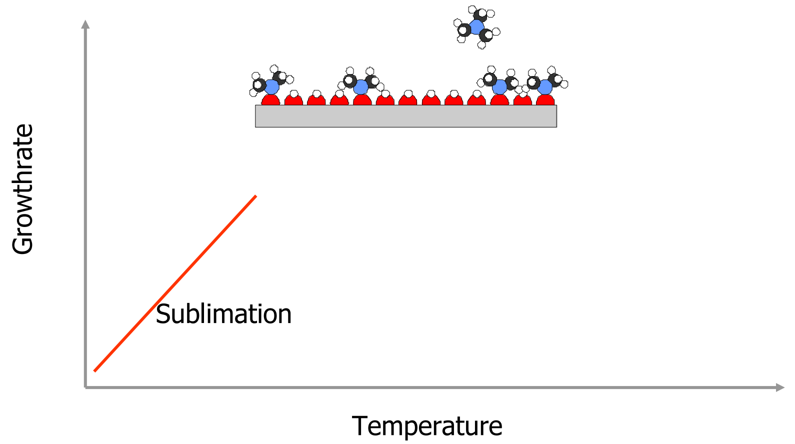
Growthkinetics



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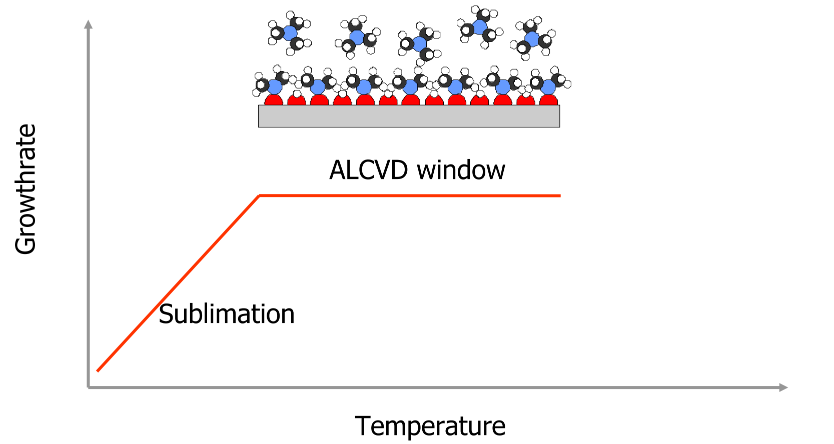
Growthkinetics



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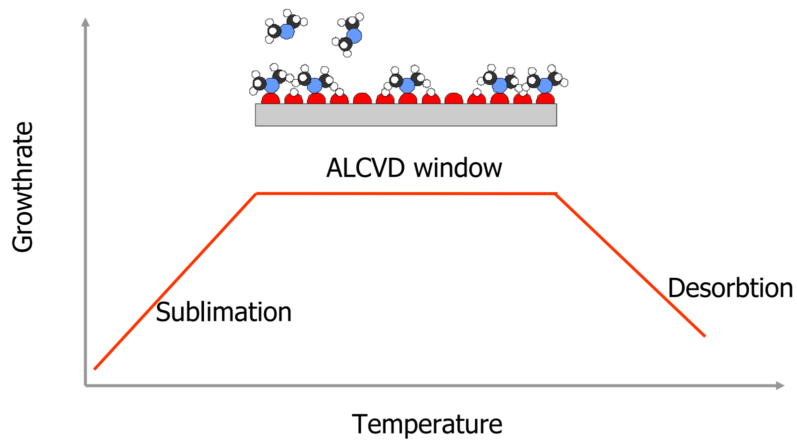
Growthkinetics



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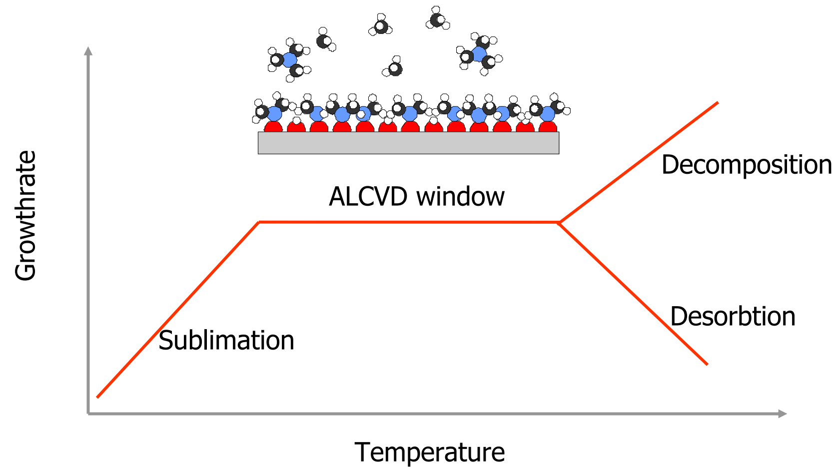
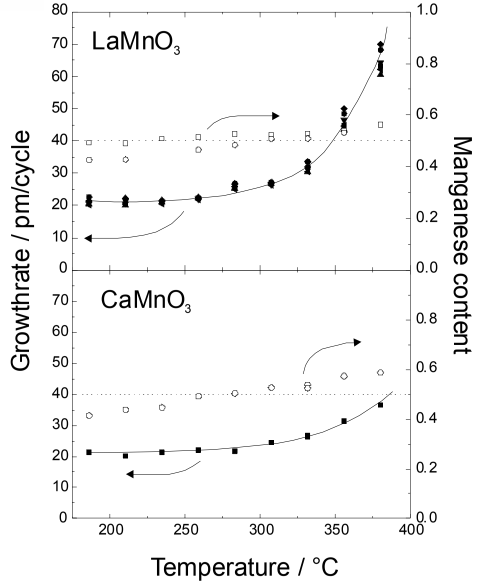
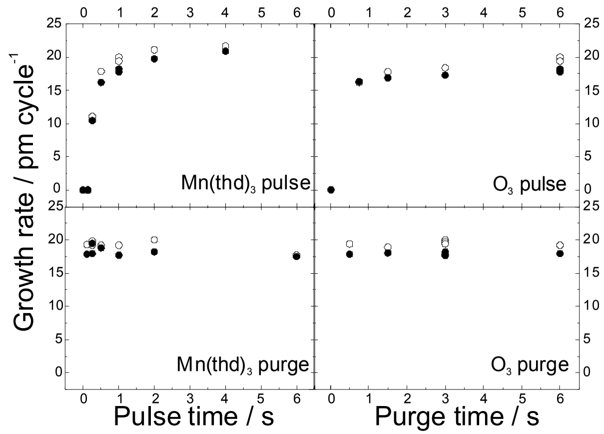
Growthkinetics



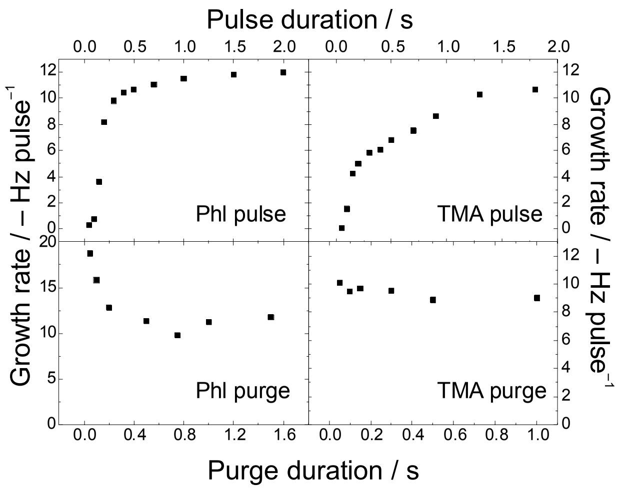
ALCVD window



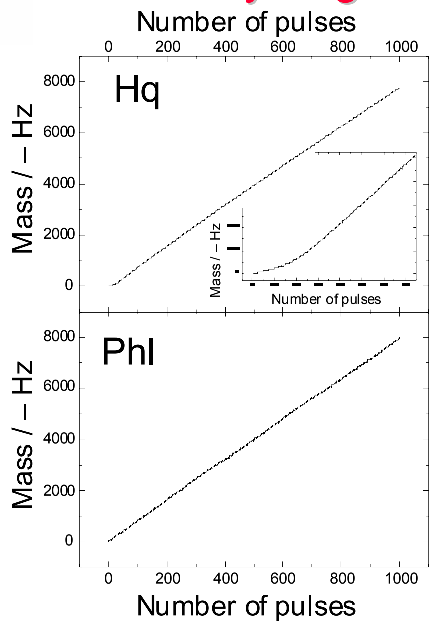
Pulse parameters



Pulsing parameters



Linearity of growth



Surface coverage

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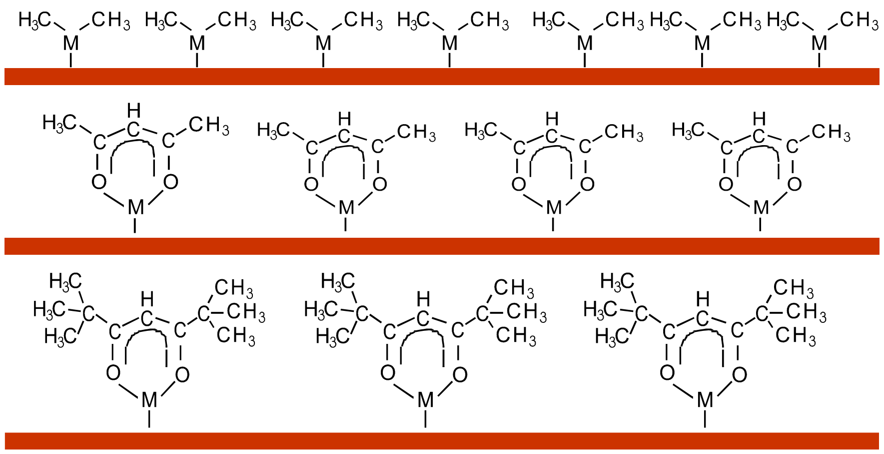

Precursor requirements

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ALCVD	CVD
-Highly reactive	-Limited reactivity
-Gaseous, liquid or solid	-Gaseous or liquid
-Non reactive byproducts	-Non reactive byproducts
-Thermally stable under reaction conditions	-Decompose cleanly under reaction conditions
-Non toxic	-Non toxic
-Easy to handle	-Easy to handle
-Inexpensive	-Inexpensive
-Low reactor temperature	-High reactor temperature

Co(thd)$_2$

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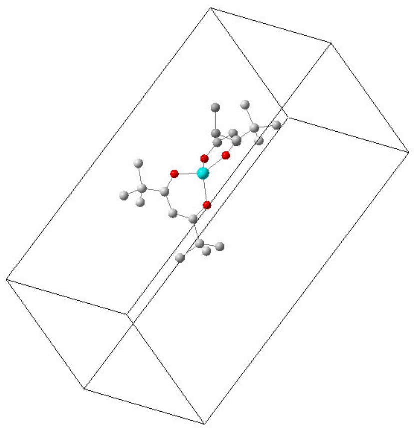

Reason for invention

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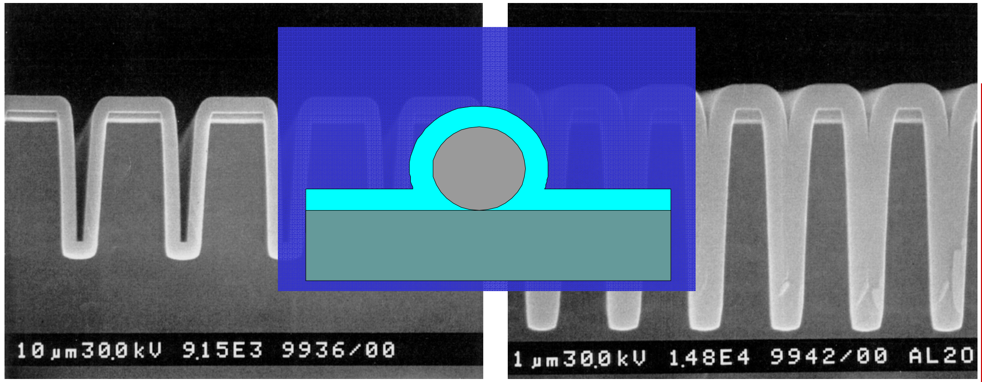
Uniform dense films



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Reaction chamber

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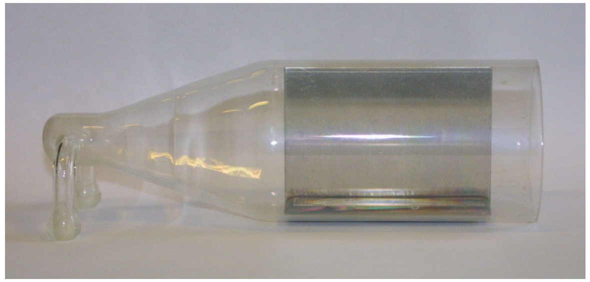

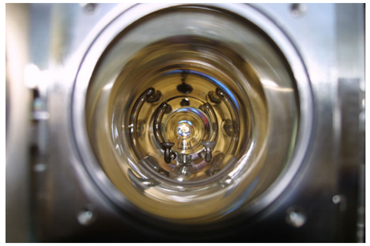

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Powder cell

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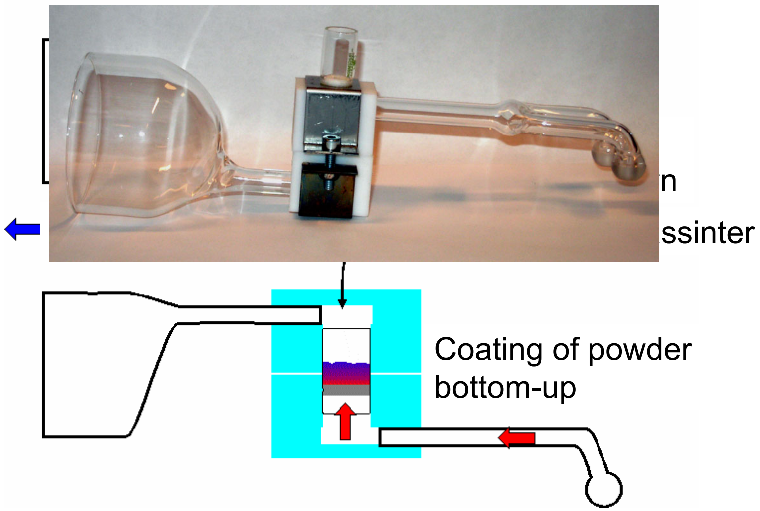

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Perovskites

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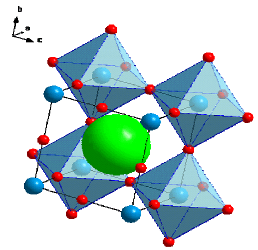

Currently grown by ALCVD:

	Compound	Reference
	$BaTiO_3$	M. Vehkamaki et al., Electrochem. Solid-State Lett. 2(1999) 504.
	Bi-Ti-O	M. Schuisky et al., Chem. Vap. Deposition, 6 (2000) 139.
●	$CaMnO_3$	O. Nilsen et al.
●	$La_{1-x}Ca_xMnO_3$	O. Nilsen et al.
●	$La_{1-x}Sr_xFeO_3$	M. Lie et al.
●	$LaFeO_3$	M. Lie et al.
	$LaAlO_3$	M. Nieminen et al. J. Mater. Chem. 11 (2001) 2340.
●	$LaCoO_3$	H. Seim et al. Appl. Surf. Sci. 112 (1997) 243.
	$LaGaO_3$	M. Nieminen et al. J. Mater Chem. 11 (2001) 3148.
●	$LaMnO_3$	O. Nilsen et al
●	$LaNiO_3$	H. Seim et al. J. Mater. Chem. 7 (1997) 449.
	$SrTiO_3$	M. Vehkamaki et al., Electrochem. Solid-State Lett. 2(1999) 504.
		A. Kosola et al., Appl. Surf. Sci. 211 (2003) 102.
		M. Vehkamaki, et al. Chem. Vap. Deposition 7 (2001) 75.

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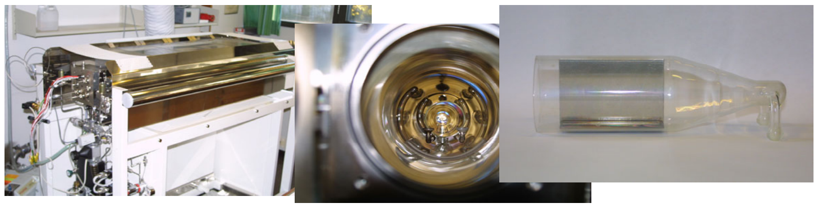
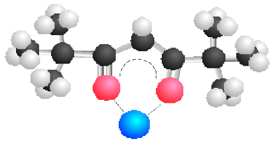
The growth of oxides

F-120 Sat reactor from ASM Microchemistry



Metal precursors:

- Ca(thd)$_2$ (Ca$_2$(thd)$_6$)
- La(thd)$_3$
- Mn(thd)$_3$



(Hthd = 2,2,6,6-tetramethylheptan-3,5-dione)

Oxygen source: O_3

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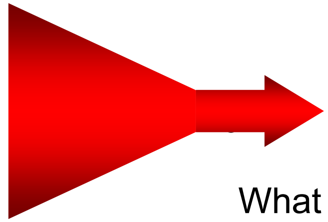
Growth of $La_{1-x}Ca_xMnO_3$

MnO_2

La_2O_3

$CaCO_3$



What about:

- Stoichiometry?
- Carbonate?
- ALD-window?

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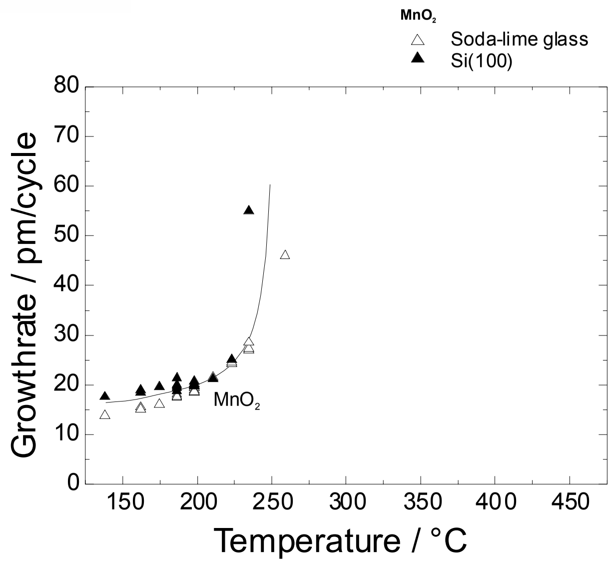
ALD-window



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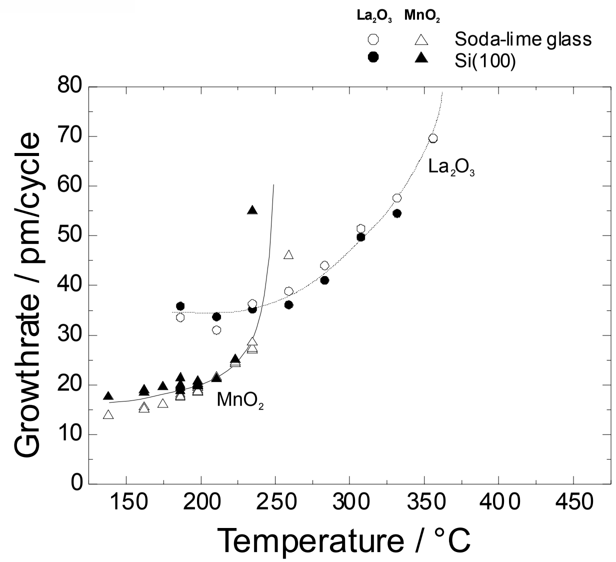
ALD-window



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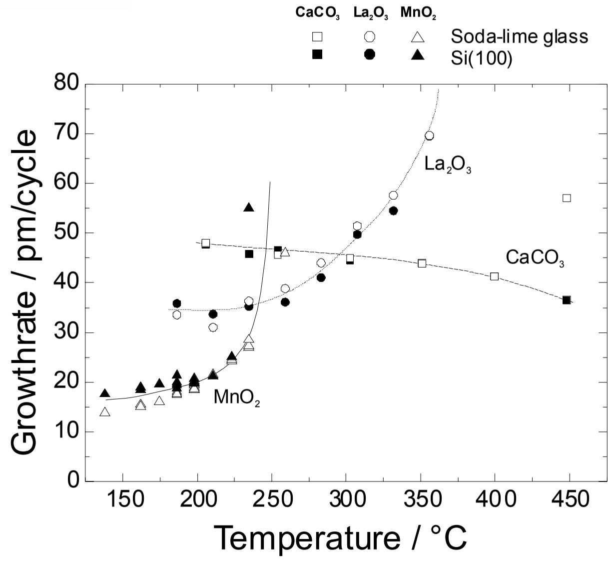
ALD-window



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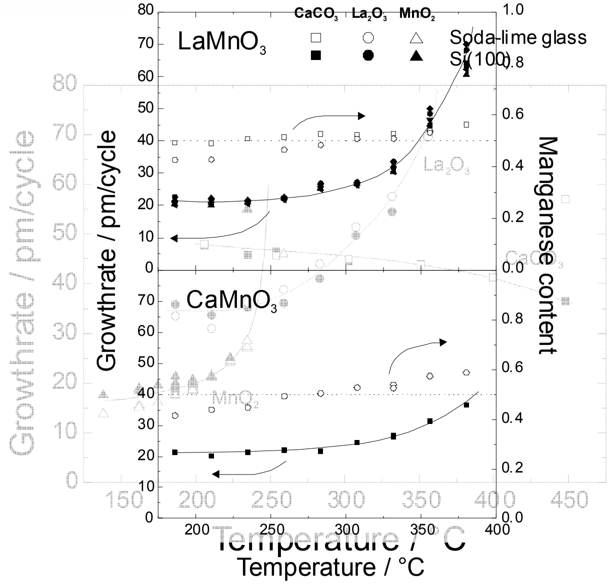
ALD-window



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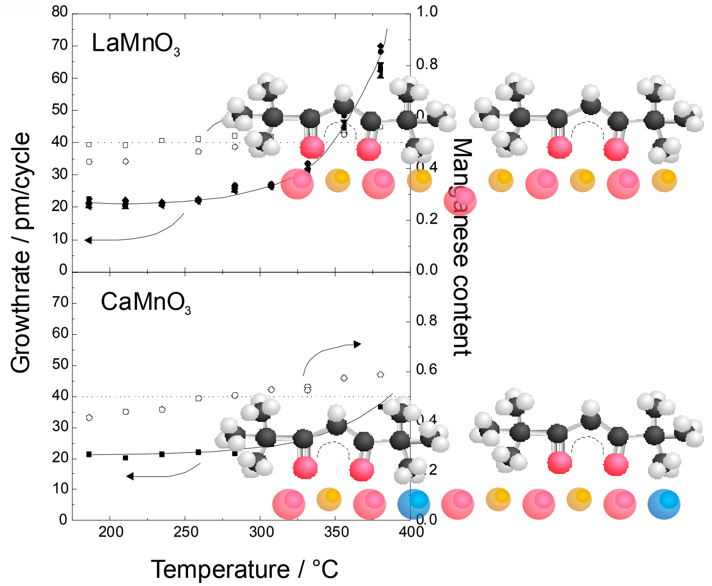
ALD-window



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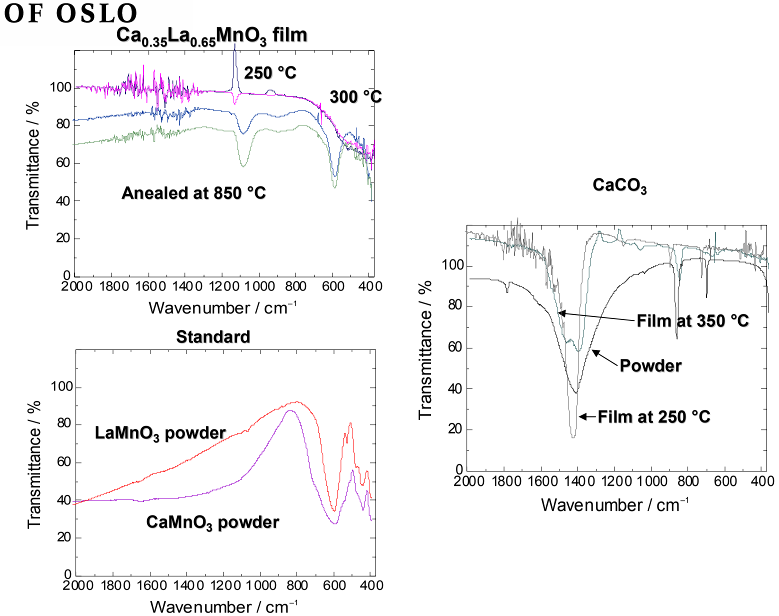
Carbonate formation?



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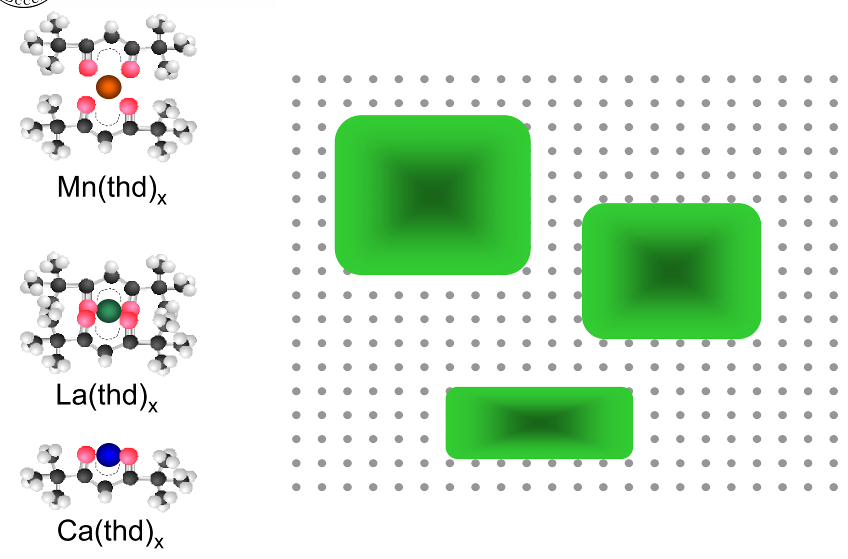
Surface utilisation



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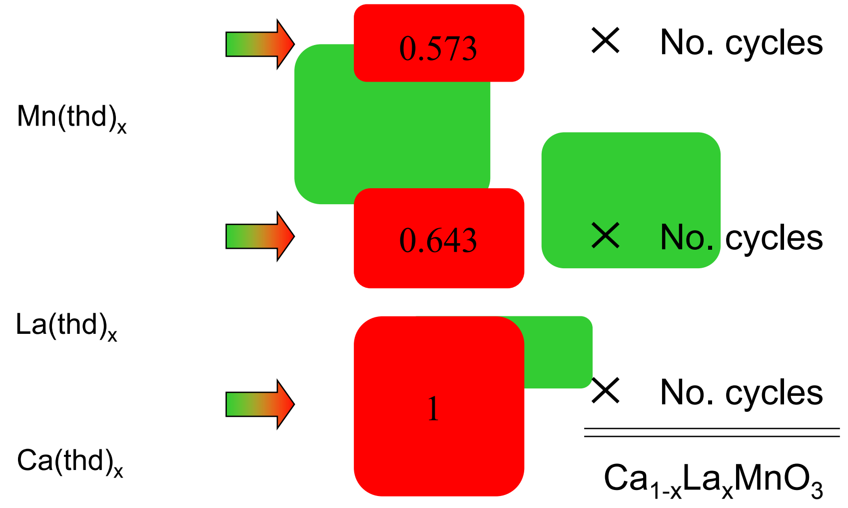
Surface utilisation



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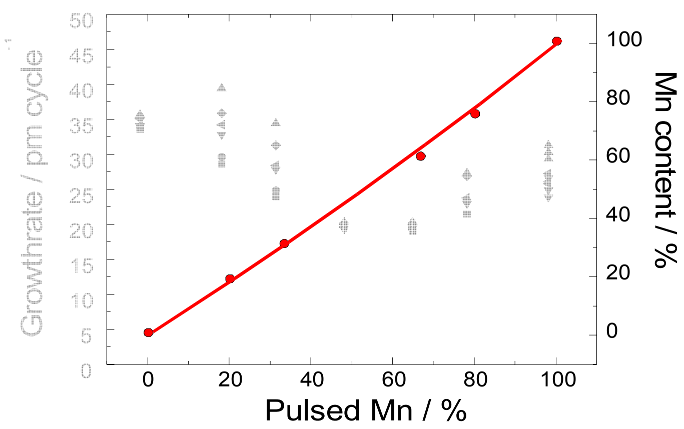
Composition

La : Mn



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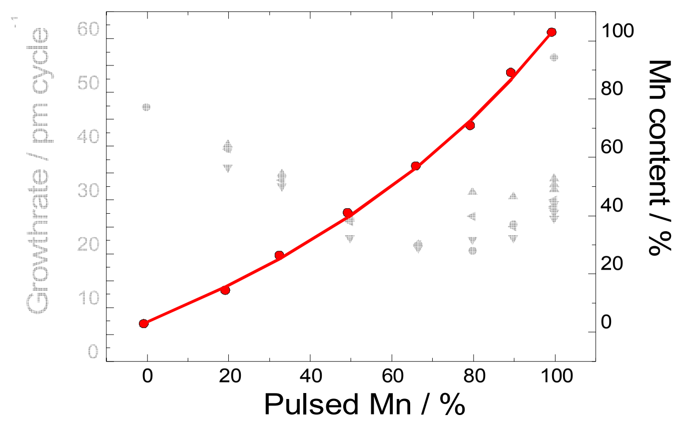
Composition

Ca : Mn



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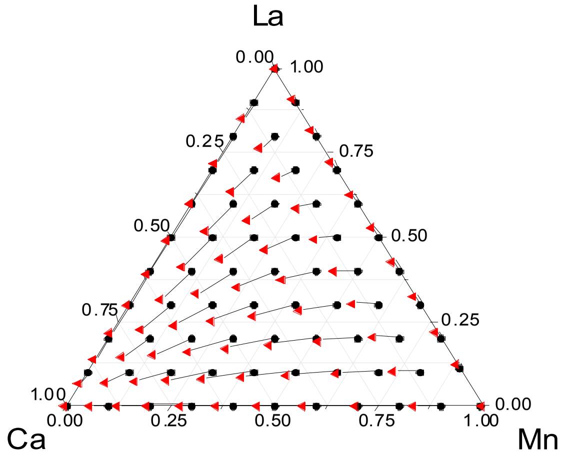
Composition



Tr = 250 °C

Ca: 1
La: 0.643
Mn: 0.573

- ● Pulsed
- ◀ Calculated

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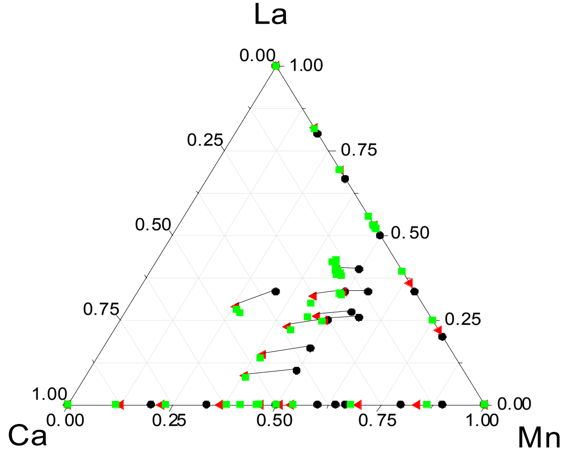
Composition



Tr = 250 °C

Ca: 1
La: 0.643
Mn: 0.573

- ● Pulsed
- ◀ Calculated
- ■ Measured

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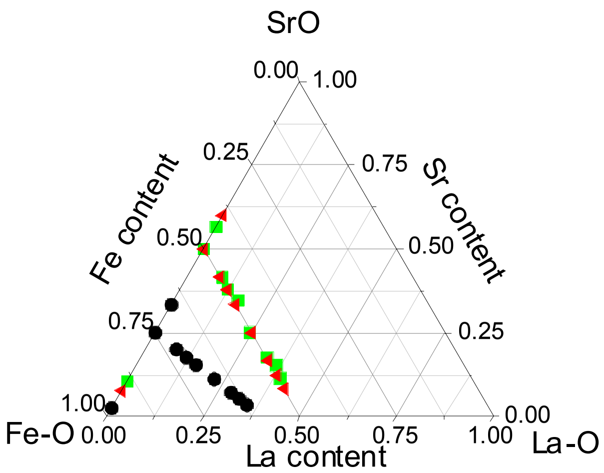
La-Sr-Fe-O



Tr = 250 °C

- ● Pulsed
- ◀ Calculated
- ■ Measured

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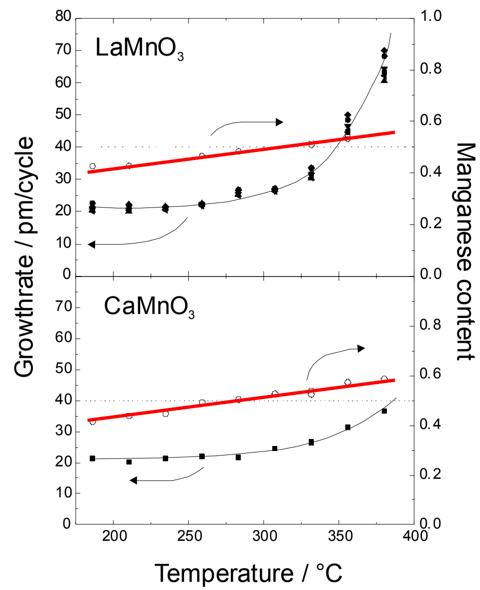
Composition - Temperature



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Composition – The runs

	Mn	La	Ca
Wanted: $Ca_{0.5}La_{0.5}MnO_3$	0.5	0.25	0.25
	0.573	0.643	1
Calculated pulsing ratio:	0.577	0.257	0.165
Practical pulsing ratio:	0.571	0.257	0.171
	0.573	0.643	1
Calculated composition:	0.493	0.249	0.258

1 cycle: 20 × Mn
9 × La
6 × Ca = 35 pulses

Tr = 250 °C

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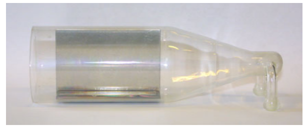
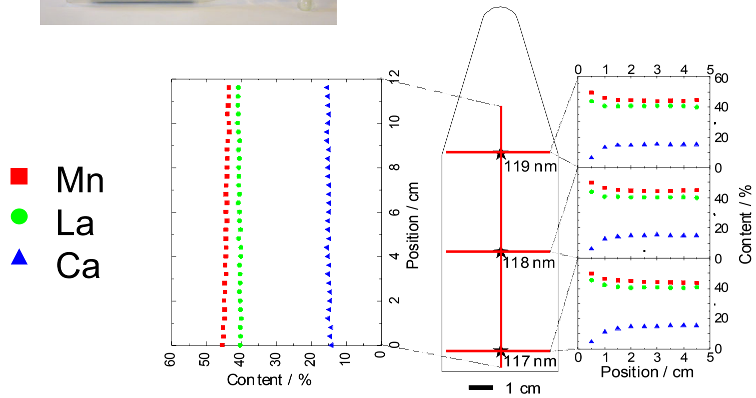
Composition – Areal variations



$Ca_{0.3}La_{0.7}MnO_3$



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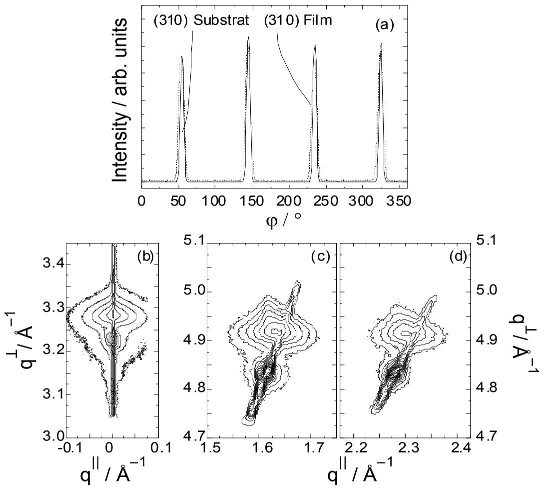
$Ca_{0.35}La_{0.65}MnO_3$ on $SrTiO_3(100)$



Tr = 300 °C

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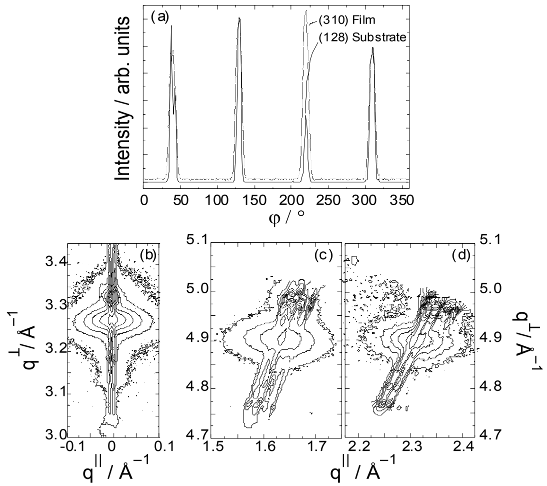
$Ca_{0.35}La_{0.65}MnO_3$ on $LaAlO_3(100)$



Tr = 300 °C

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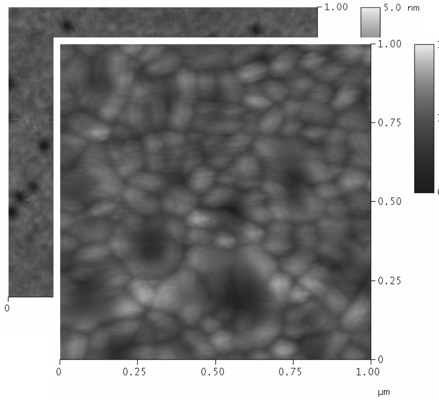
$Ca_{0.35}La_{0.65}MnO_3$ on $SrTiO_3(100)$

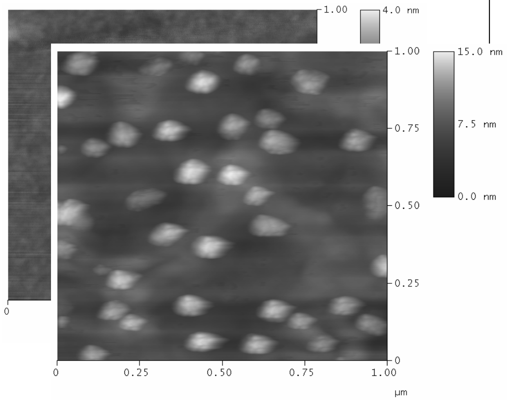
Tr = 250 °C



Rms = 0.32 nm

Rms = 1.5 nm

Tr = 300 °C



Rms = 0.16 nm

Rms = 1.9 nm

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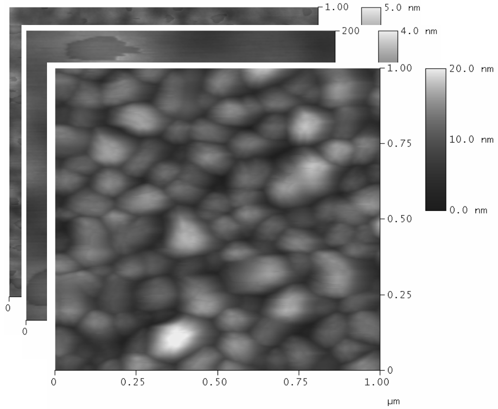
$Ca_{0.35}La_{0.65}MnO_3$ on MgO(100)

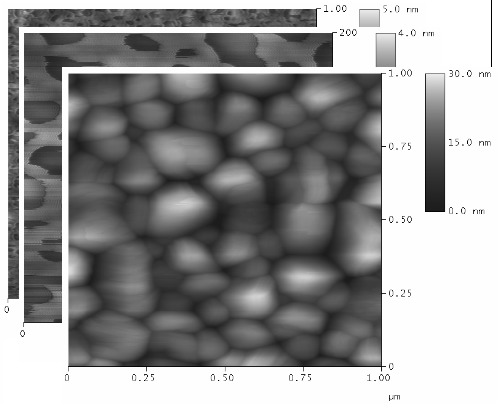
Tr = 250 °C



Rms = 0.37 nm

Rms = 3.0 nm

Tr = 300 °C



Rms = 0.53 nm

Rms = 5.2 nm

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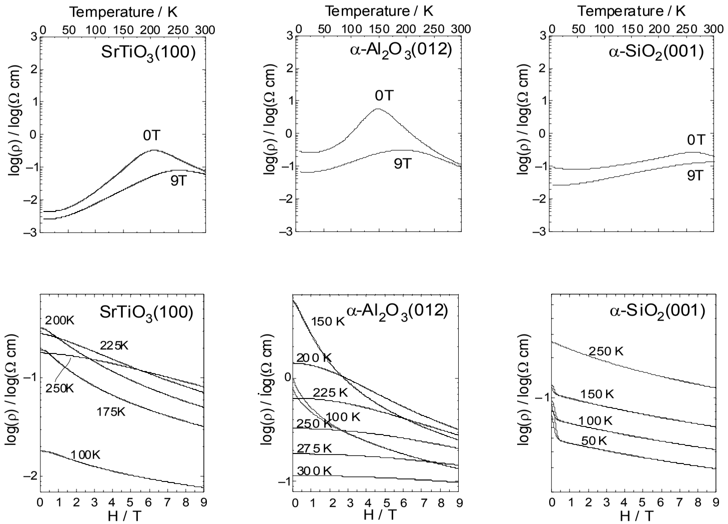
Colossal magnetoresistance



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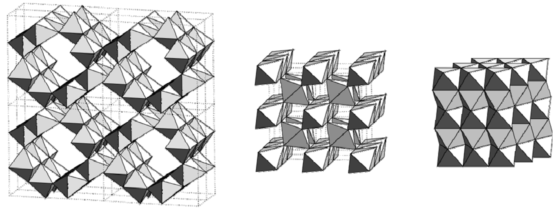
Effects of substrate

Grown film on substrates of:

Soda-lime glass
Si(100)
Kapton™ foil
α-SiO_2(001)
α-Al_2O_3(012)
α-Al_2O_3(001)
Muscovite(001)
MgO(100)
NaCl(100)
KCl(100)
KBr(100)
KI(100)

Obtained phases of:

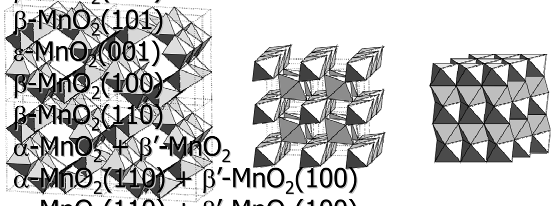


α-MnO_2 β-MnO_2 ε-MnO_2

β'-MnO_2

Effects of substrate

Grown film on substrates of:	Obtained phases of:
Soda-lime glass	β'-MnO_2(100)
Si(100)	β'-MnO_2(100)
Kapton[TM] foil	β-MnO_2
α-SiO_2(001)	β-MnO_2(100)
α-Al_2O_3(012)	β-MnO_2(101)
α-Al_2O_3(001)	ε-MnO_2(001)
Muscovite(001)	β-MnO_2(100)
MgO(100)	β-MnO_2(110)
NaCl(100)	α-MnO_2 + β'-MnO_2
KCl(100)	α-MnO_2(110) + β'-MnO_2(100)
KBr(100)	α-MnO_2(110) + β'-MnO_2(100)
KI(100)	α-MnO_2



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MnO_2 on Al_2O_3

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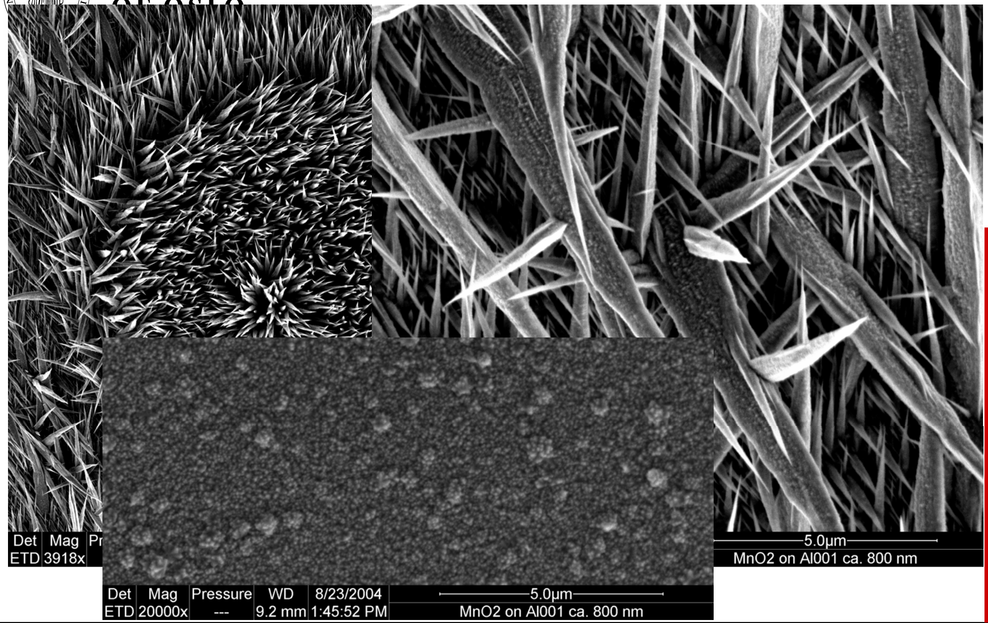

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Growthdynamics

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