Willkommen
Welcome
Bienvenue

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Materials Science and Technology

Déposition séléctive – le rêve reviens

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Michael Reinke, Yury Kuzminykh

Ivo Utke, Carlos Guerra-Nunez, ...

Ali Dabirian, Xavier Multone, Tristan Bret, Estelle Halary-Wagner, Giacomo Benvenuti, ...

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Historical

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Precursor design and selective aluminum CVD

K Tsubouchi and K Masu, *Research Institute of Electrical Communication, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980–77, Japan*

revised version received 15 December 1994

Area-selective Al CVD technology has an excellent potential for filling via and contact holes of multilevel interconnection in Si ULSI. In this article, we discuss the selective Al CVD using metalorganic sources of trimethylaluminum [$(CH_3)_3Al$, TMA] and dimethylaluminum hydride [$(CH_3)_2AlH$, DMAH]. In order to deposit Al from TMA, the TMA molecule should be selectively excited into a reactive species of $(CH_3)_2Al$ in the well controlled H_2/rf plasma. When using DMAH and H_2, Al can be deposited by low-pressure CVD; the features are (1) single crystal Al on Si surface, (2) filling capability into 0.3 μmϕ/1 μm-deep contact holes, (3) low

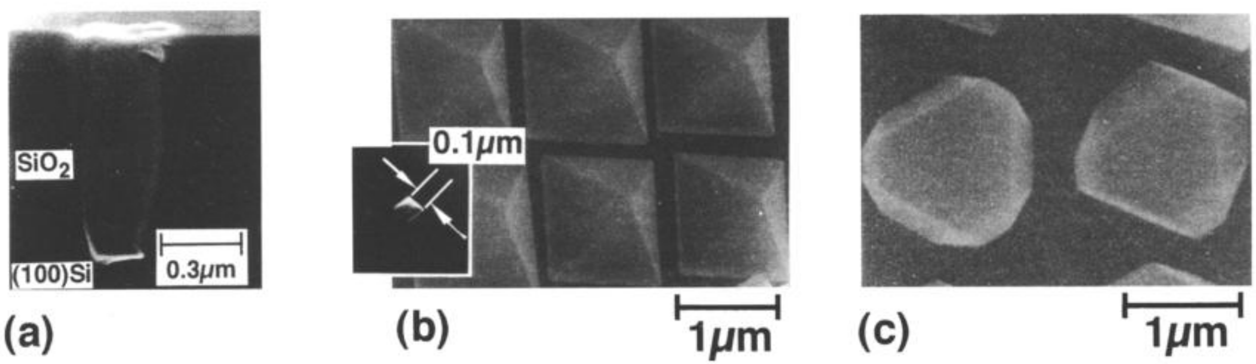


Figure 5. SEM photographs of selectively deposited Al into via holes using DMAH. In this case, plasma was not used. (a) Al in a 0.3 $\mu m\phi$ diameter via hole, (b) (100)Al on (111)Si, and (c)(111)Al on (100)Si. In (b) and (c), Al was intentionally overgrown after filling the via holes. The diameter and depth of the via holes are 0.8 and 1 μm, respectively. The insert of (b) is a 0.1 μm pyramid of Al.

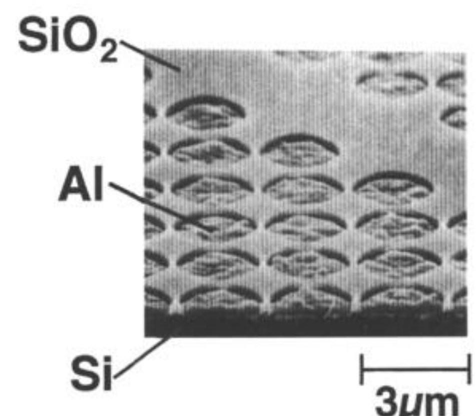
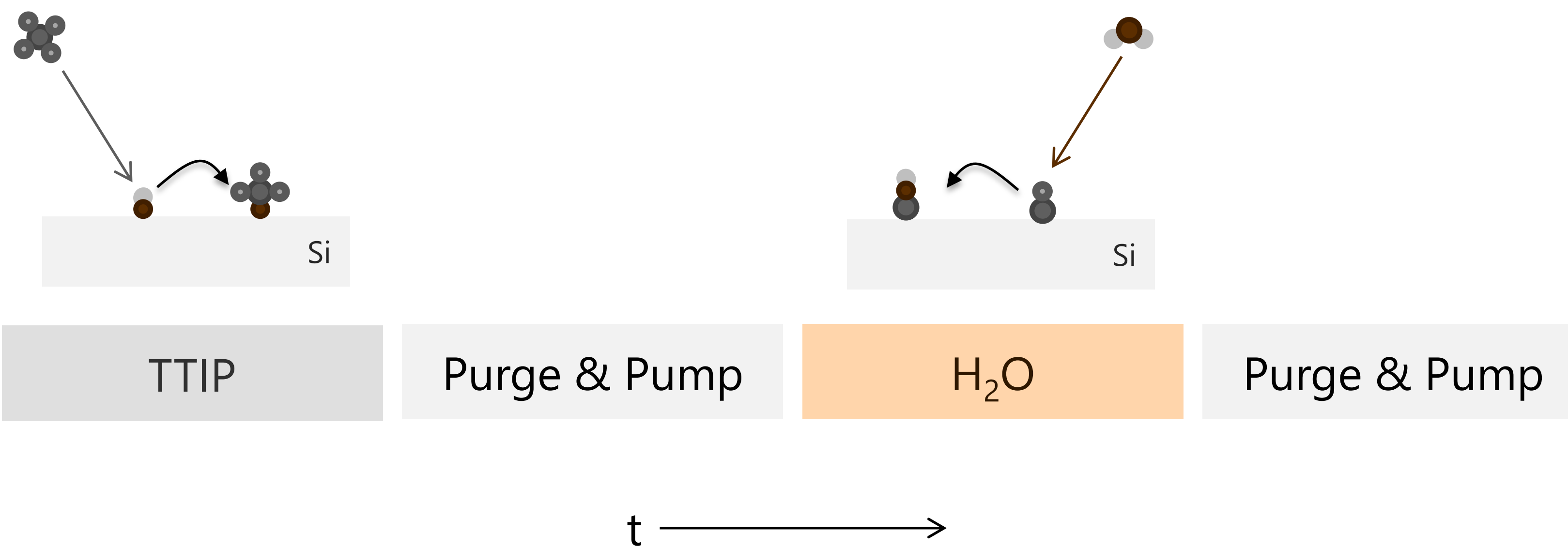
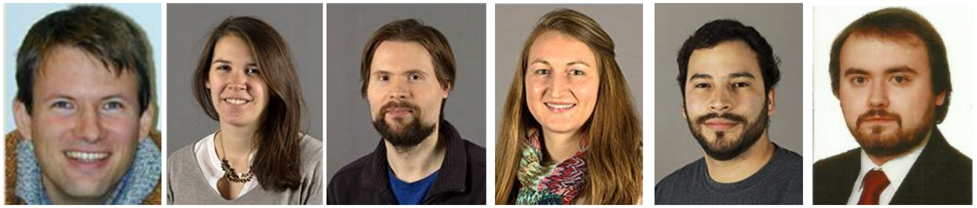


Figure 4. Selectively deposited Al into SiO_2 windows using the selectively excited TMA. The thickness of Al is 3000 Å.

What's new in ALD

Top notch at Empa





Low Dimensional Materials Group

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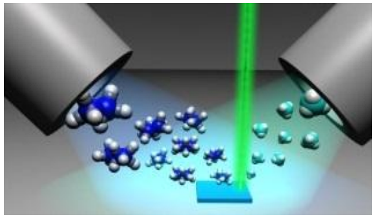
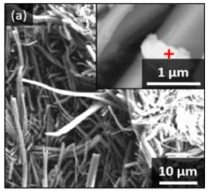
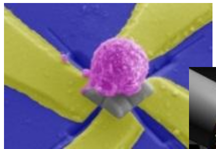
Synthesis via charged particle beams, ALD, PVD



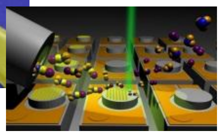
Modelling e-beam induced Additive Manufacturing



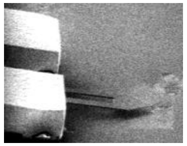
Novel precursors for Ag and Ru 3D deposition (photonics)



Hall sensors

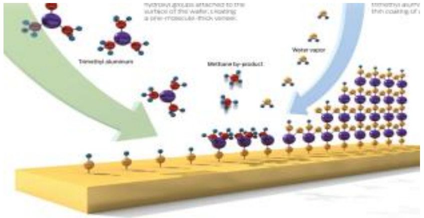


Telecom Laser Gratings

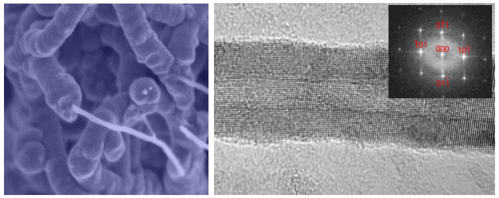


AFM in SEM

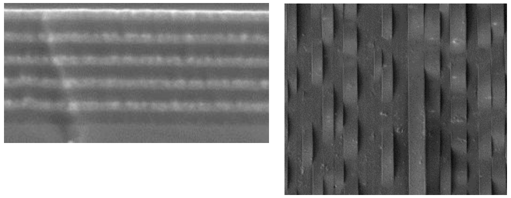
GIS in SEM



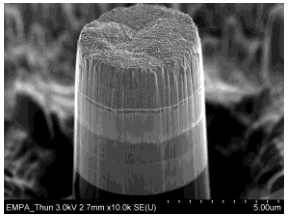
Low-T ALD development ZnO / Al2O3 TiO2 / Y2O3 /SiO2 / Cu / MgF2



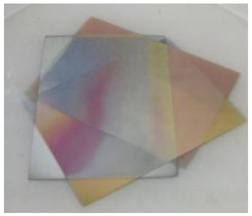
ALD Nucleation control on MW-CNTs



Oxide ALD multilayers on flexible polymers



PVD of model materials



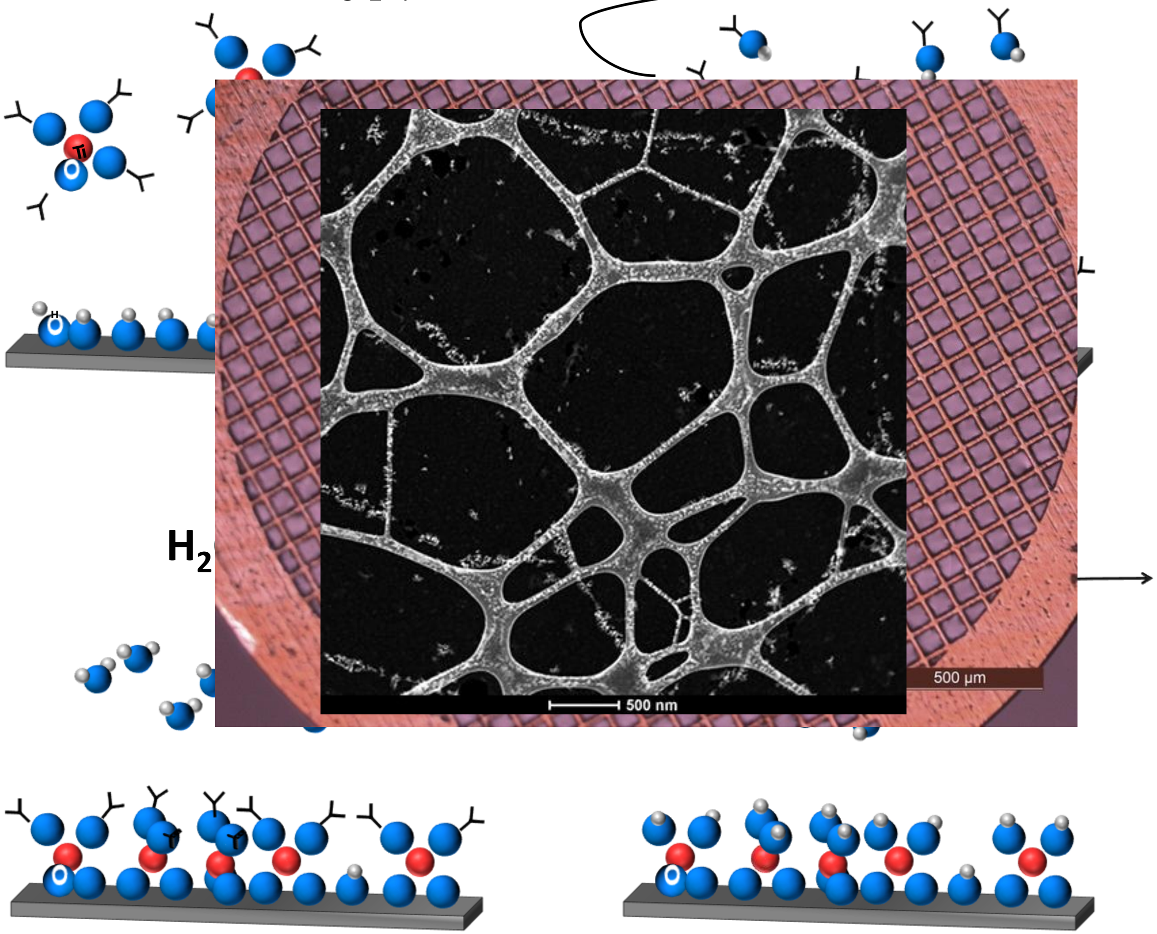
Combinatorial PVD & ALD

Atomic Layer Deposition of TiO_2

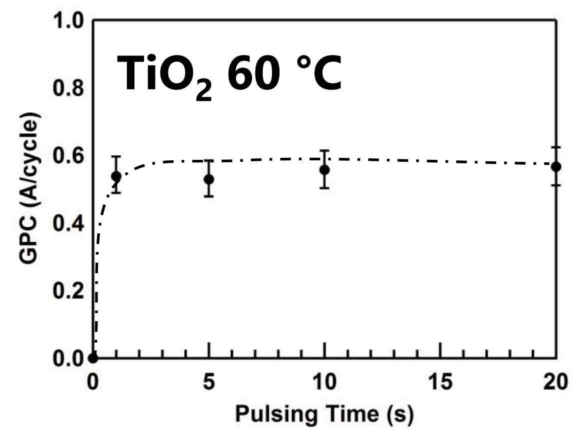
TTIP Pulse

$Ti(OCH(CH_3)_2)_4$

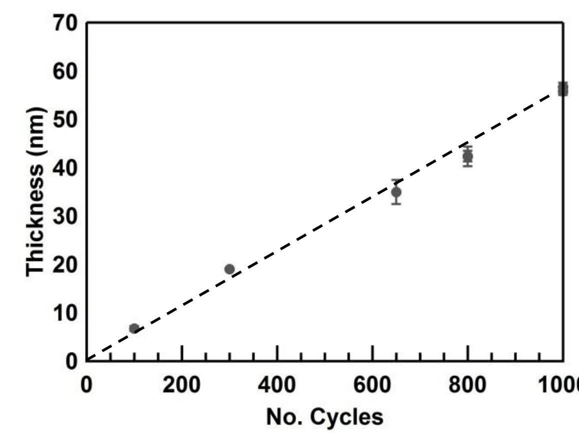
Purge



Self-limiting



Linear Growth



$Ti(OCH(CH_3)_2)_4 + 2H_2O \rightarrow TiO_2 + 4CH(CH_3)_2OH$

Early stage nucleation on SLG/FLG

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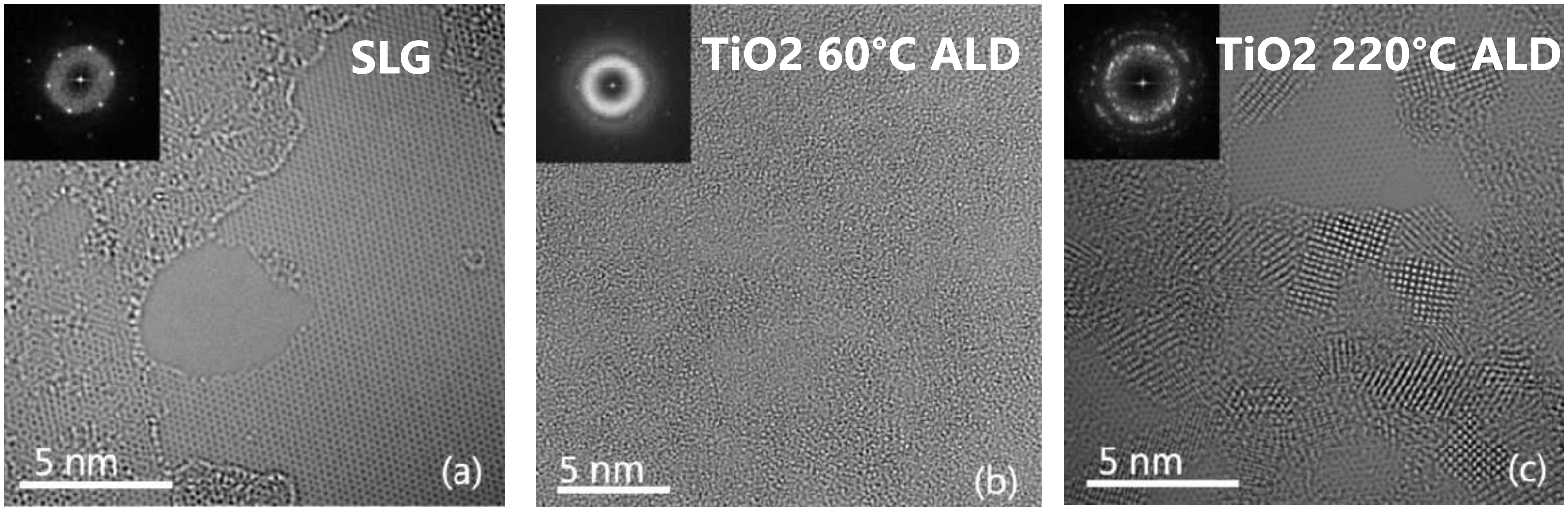
STEM at 80 kV

Pristine sample

20 cycles of ALD TiO_2



Areas of few 100 nm^2 of SLG

FLG and a:C residues

Fully covered by amorphous TiO2

-Anatase crystals ≈2 nm size

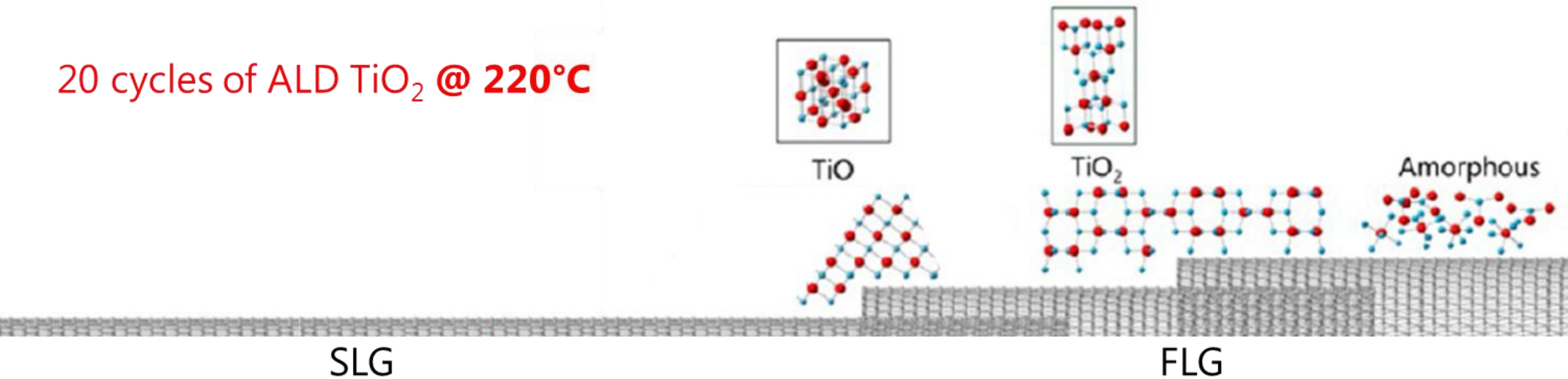
-Nucleating @ the few-layer graphene and contamination regions

-Clean SLG pristine region largely free of nucleation.

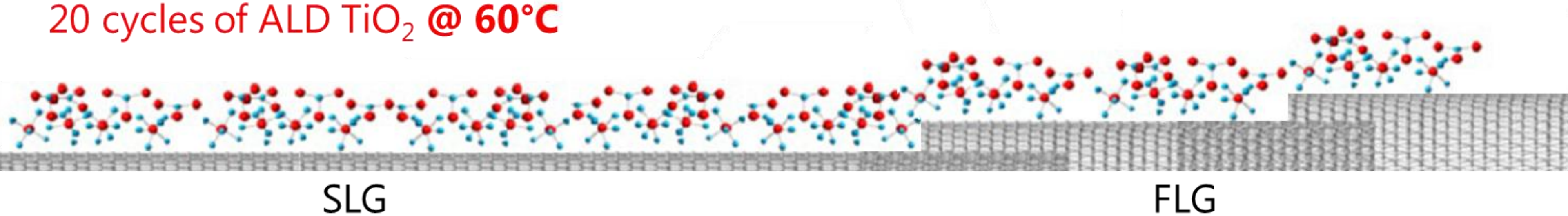
Y. Zhang, C. Guerra-Nunez et al. (2017): Atomic Layer Deposition of Titanium Oxide on Single Layer Graphene: an Atomic Scale Study towards Understanding Nucleation and Growth, Chemistry of Materials, DOI: 10.1021/acs.chemmater.6b05143

Early stage nucleation on graphene

20 cycles of ALD TiO_2 **@ 220°C**



20 cycles of ALD TiO_2 **@ 60°C**



@ 20 cycles: titanium oxide is present mostly in reduced form at early stage ALD for 60°C and 220°C

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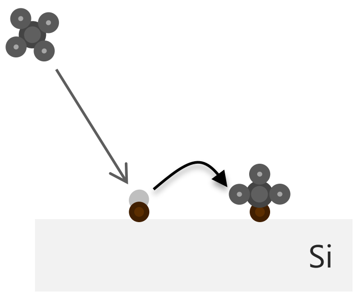
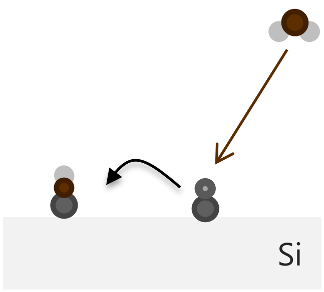
A typical ALD process with two precursors





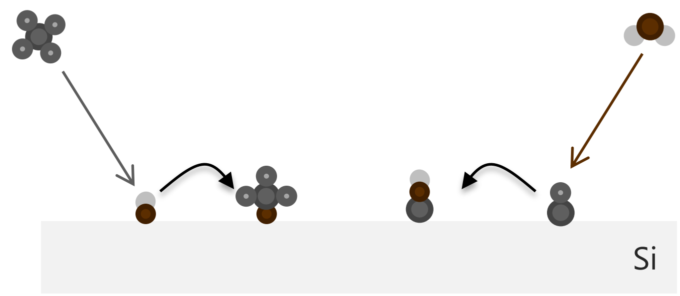
TTIP	Purge & Pump	H_2O	Purge & Pump

t →

growth process is driven by surface reactions

no gas phase interactions

What happens if we change a bit?



TTIP + H_2O

Pump, Pump, Pump

growth process is driven by surface reactions

no gas phase interactions

High Vacuum Chemical Vapor Deposition (HV-CVD)

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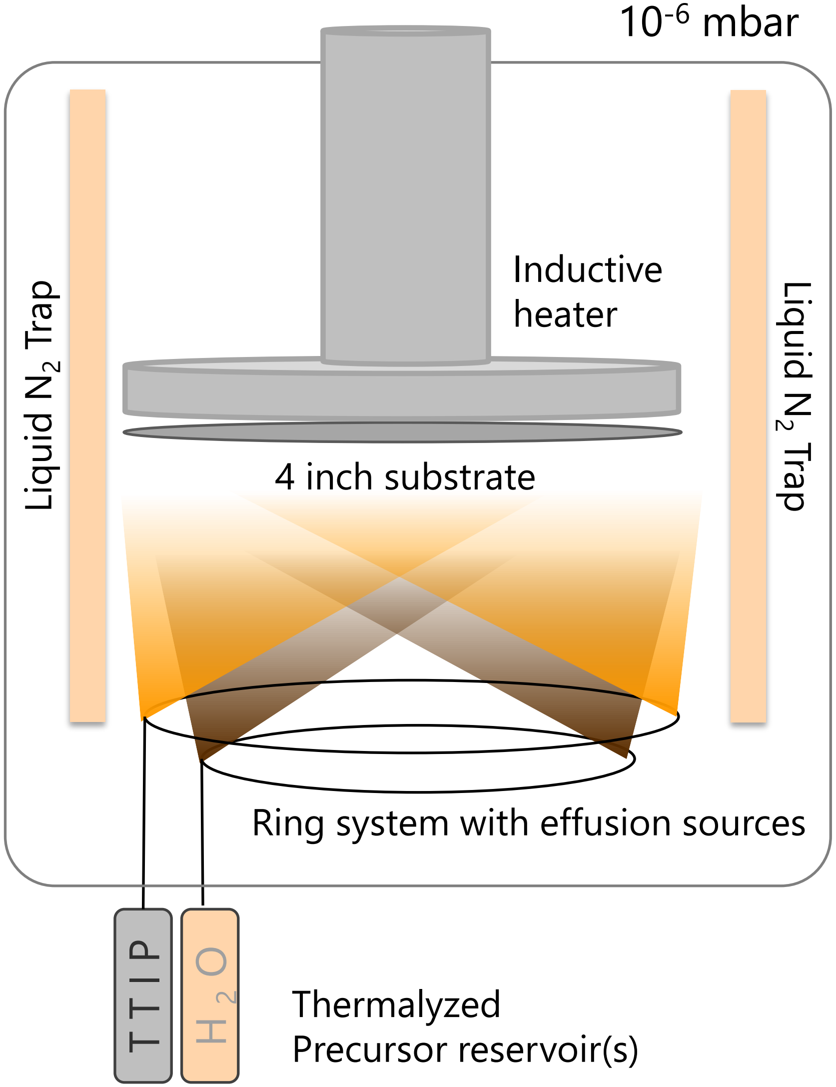


- No precursor interaction during precursor transport to the substrate
- Predictable (and controllable) precursor impinging rates

Kuzminykh, et al., Surface and Coatings Technology, 2013, http://dx.doi.org/10.1016/j.surfcoat.2013.06.059

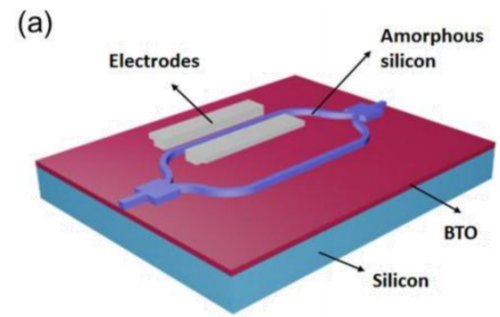
Deposition of electro-optic thin films

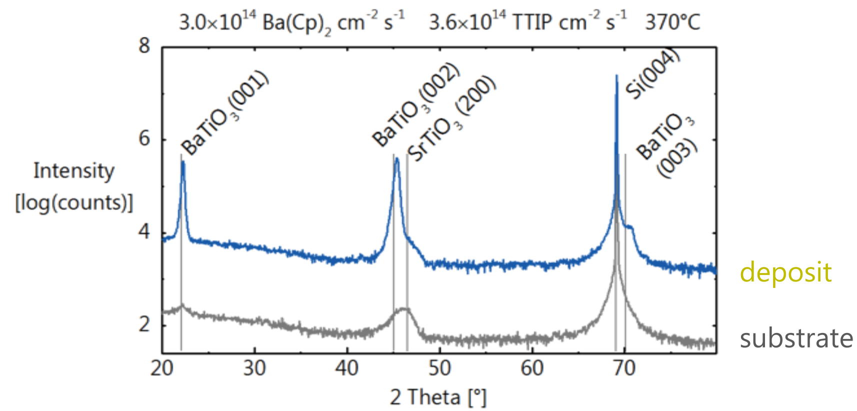
Team involved: Michael Reinke, Muriel Blum, Yury Kuzminykh, Patrik Hoffmann

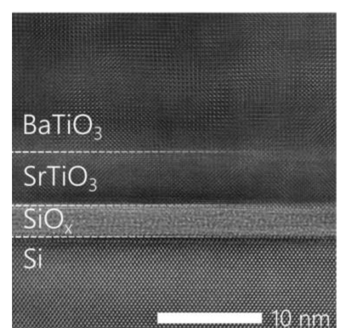
- $BaTiO_3$ is a promising material for active electro-optic switches for integrated photonic circuits

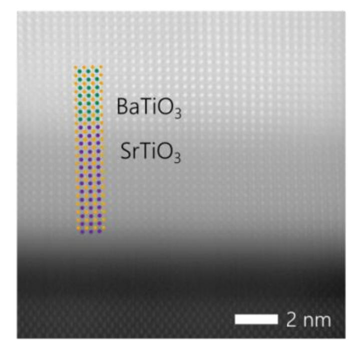
- HV-CVD was used to deposit epitaxial barium titanate on buffered silicon at 400°C –
  - **compatible with todays CMOS technology**

- The electro-optic coefficient is currently optimized, highest values so far ~150pm/V
  - Comparable to values of films grown by MBE at 600°C

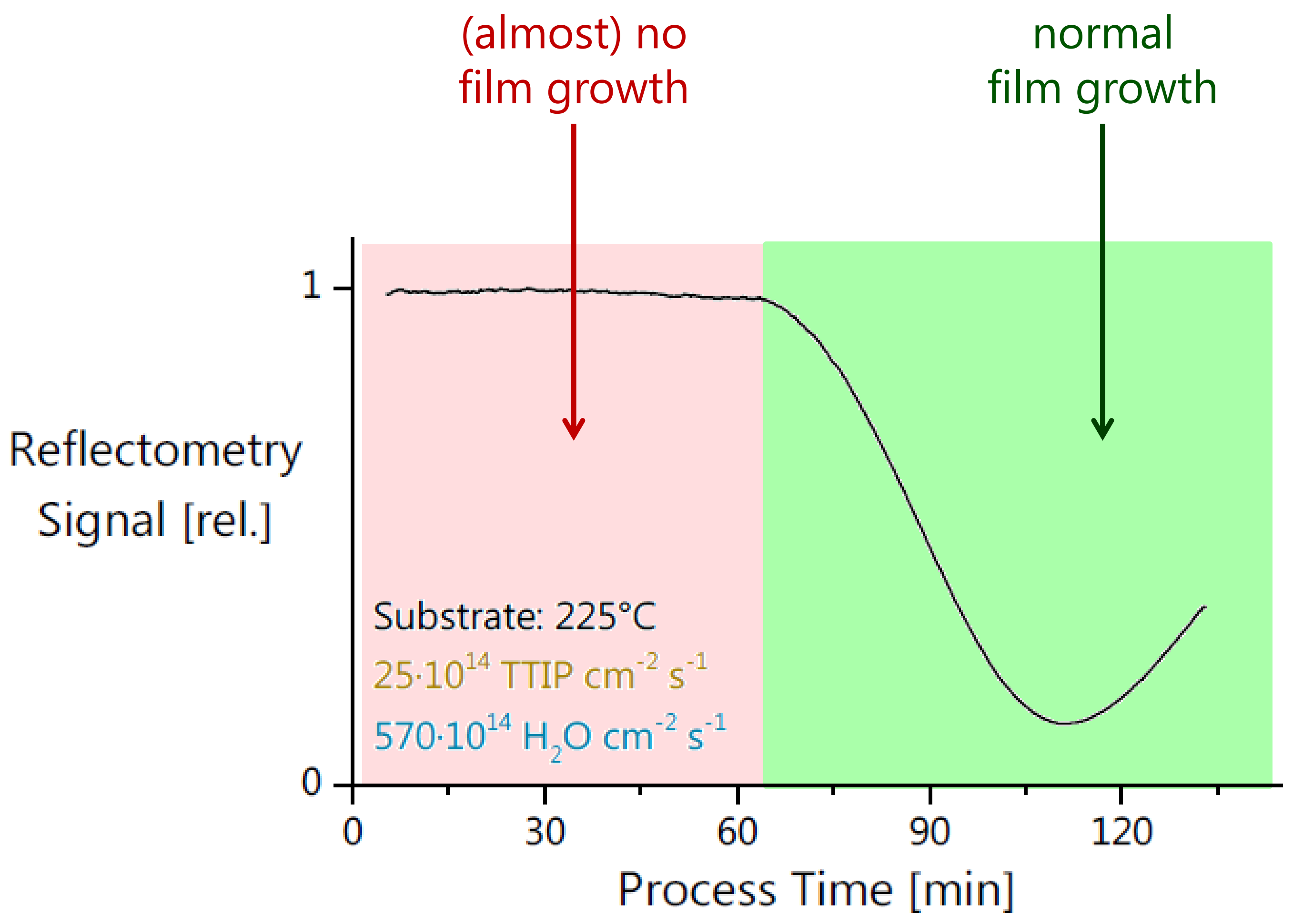




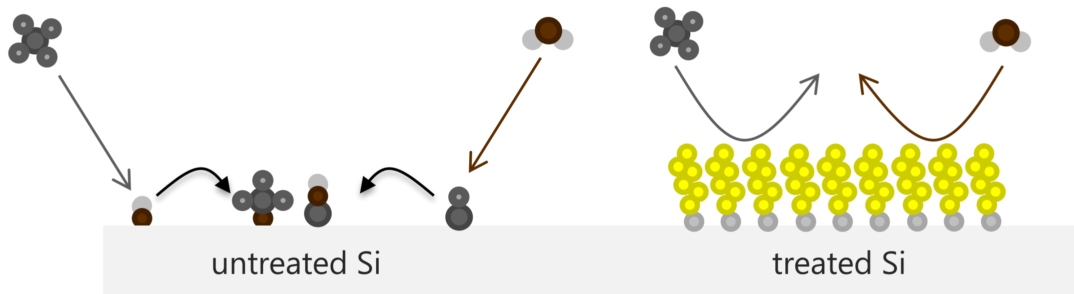




Film growth starts after an incubation period



How to achieve selectivity?

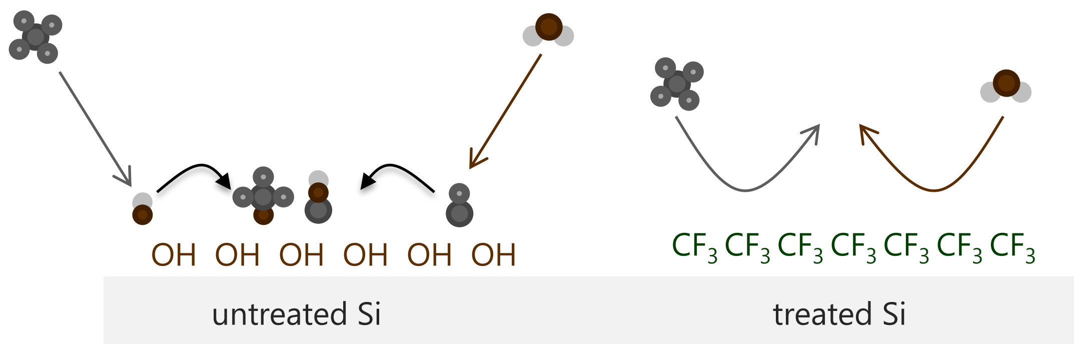


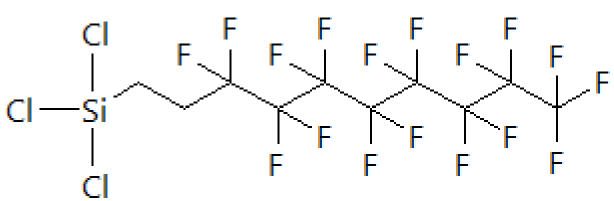
TTIP + H_2O

Pump, Pump, Pump

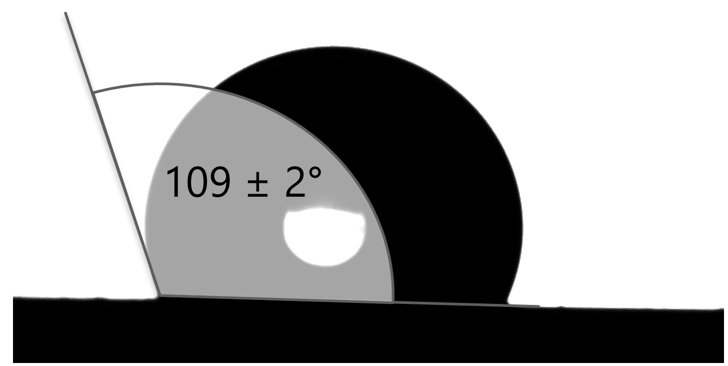
surface deactivation by pre-patterned self assembled monolayer

PTFS Patterning changes the surface chemistry





PFTS
(Perfluorodecyltrichlorosilane)



Water contact angle on treated surface

After PFTS treatment the surface is rendered hydrophobic
e.g. the sticking coefficient for the precursors is decreased

Incubation Time Difference is Measured by Reflectometry

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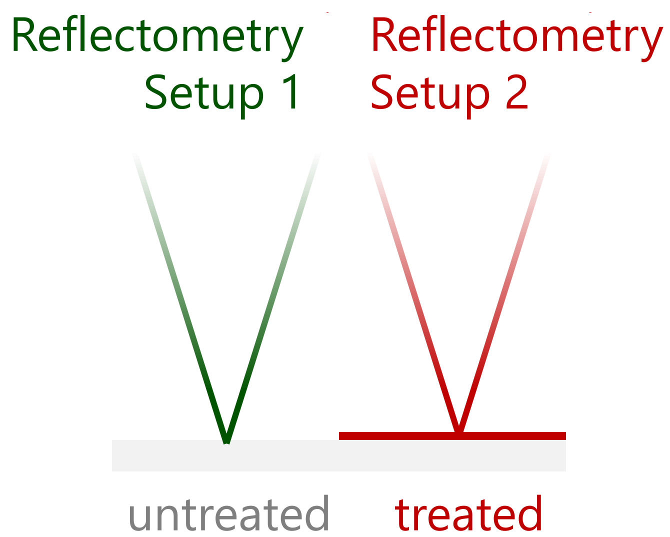
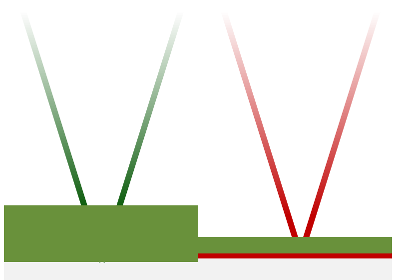
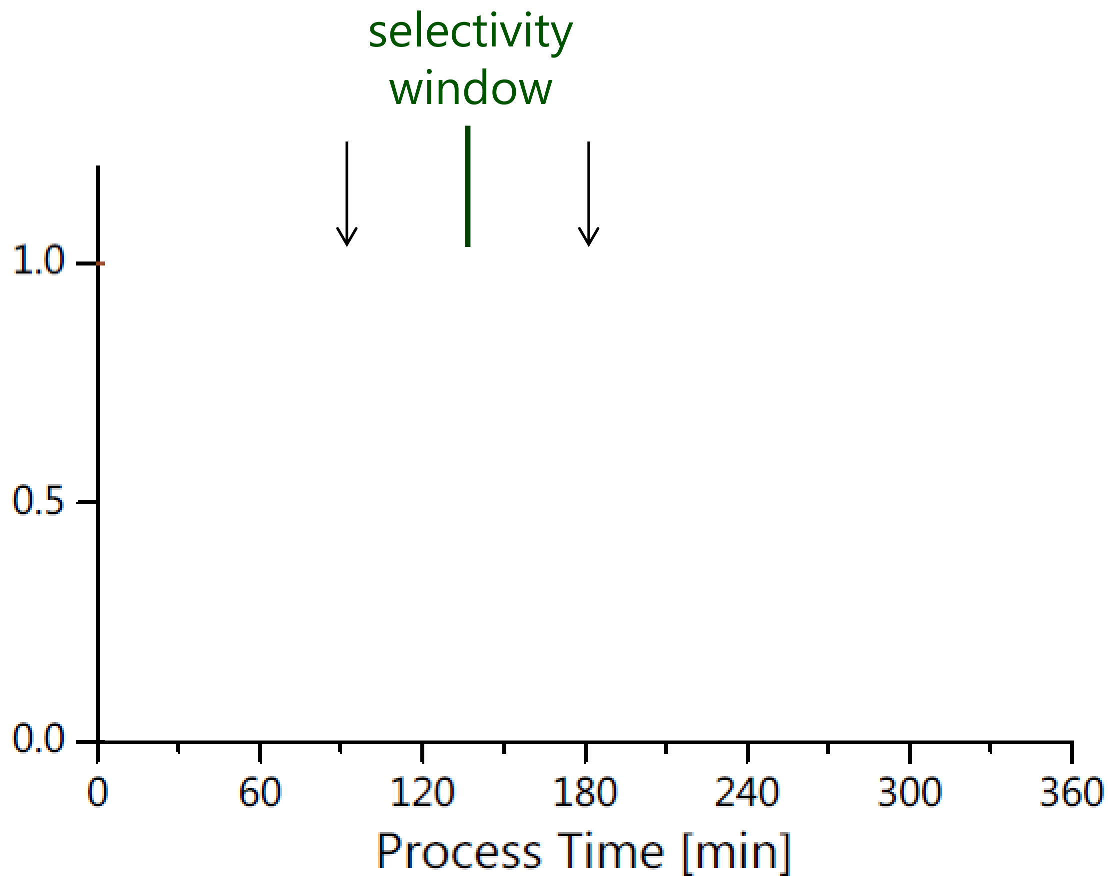


Incubation time on
treated and untreated surfaces
are measured simultaneously

Incubation Time Difference is Measured by Reflectometry



Substrate: 225°C
TTIP exposure: $3 \cdot 10^{14}$ cm^{-2} s^{-1}
H_2O exposure: $570 \cdot 10^{14}$ cm^{-2} s^{-1}



The Incubation Time depends on the Precursor Dosage

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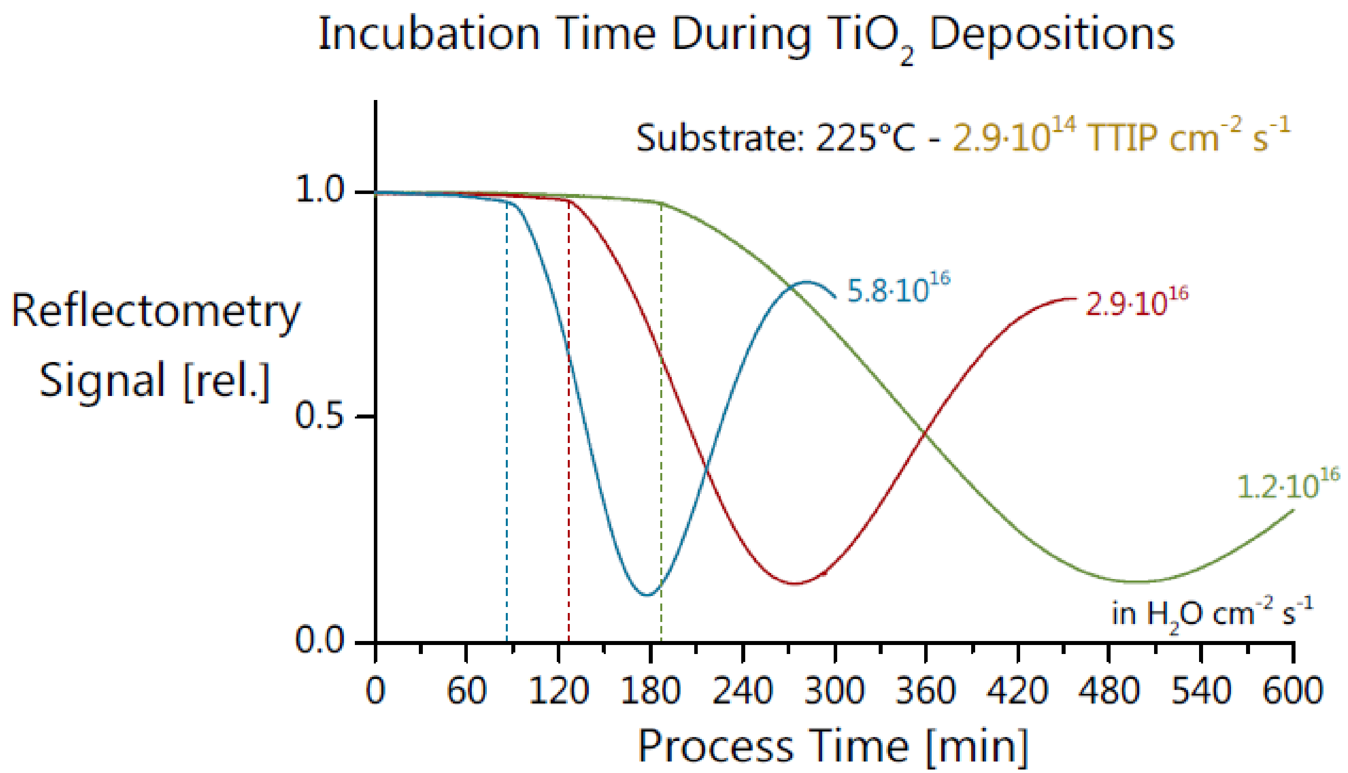
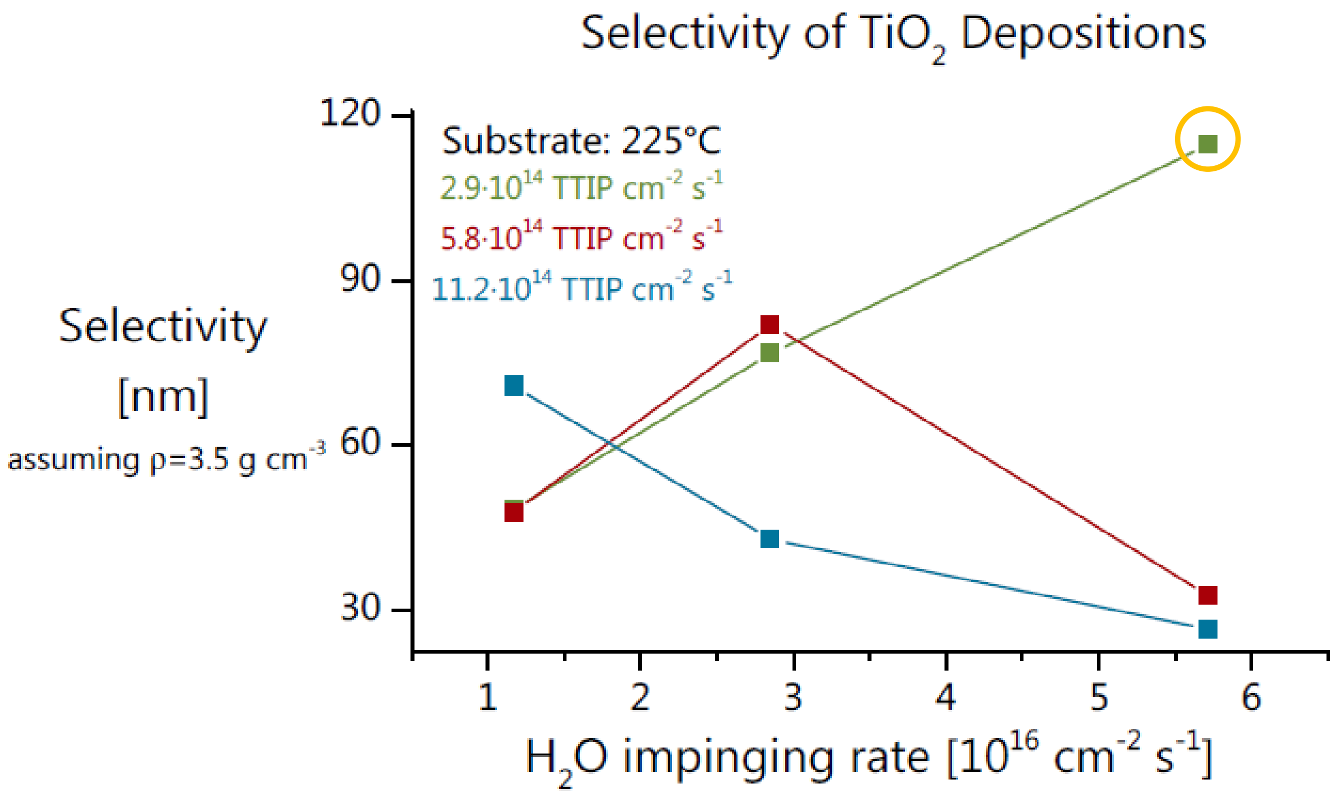


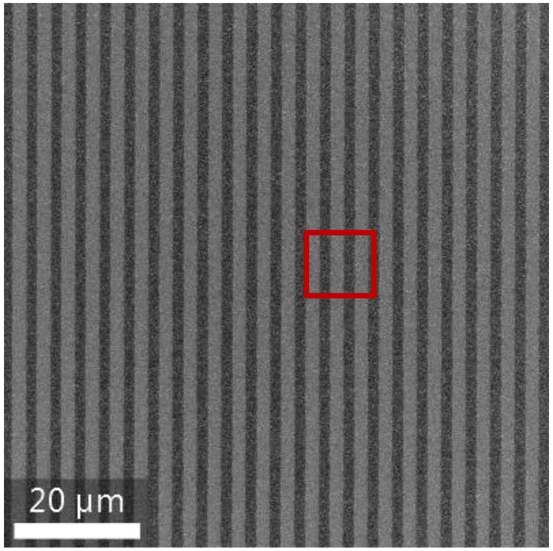
for the given TTIP dosage,
the incubation time strongly depends on the H_2O dosage

Selectivity depends on Incubation Time and Growth Rate



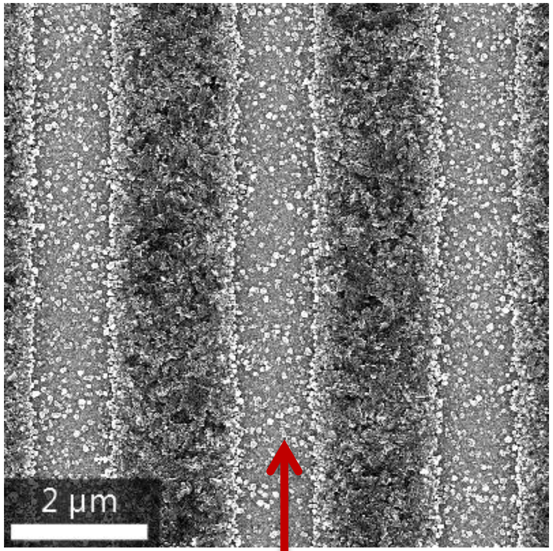
The best selectivity is reached at high H_2O and low TTIP dosages

TiO_2 Growth is Surpressed on the Treated Surface Regions



2µm lines ▪ 2µm spacing

Si (substrate) TiO_2



TiO_2 nucleation sites as consequence of

- Overexposure during deposition
- Non perfect SAM layer

Smaller Features are obtained by E-Beam Lithography

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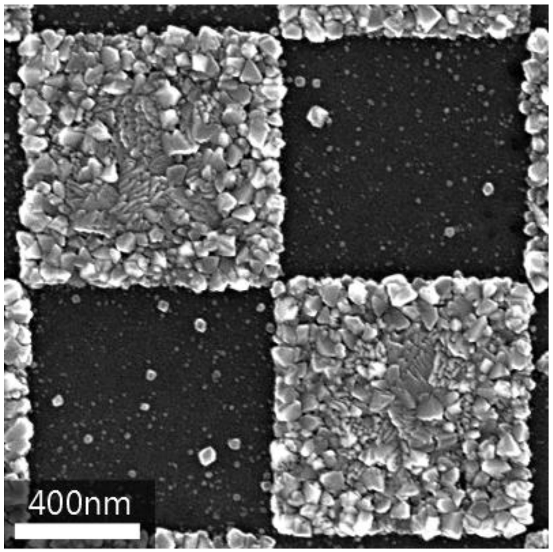
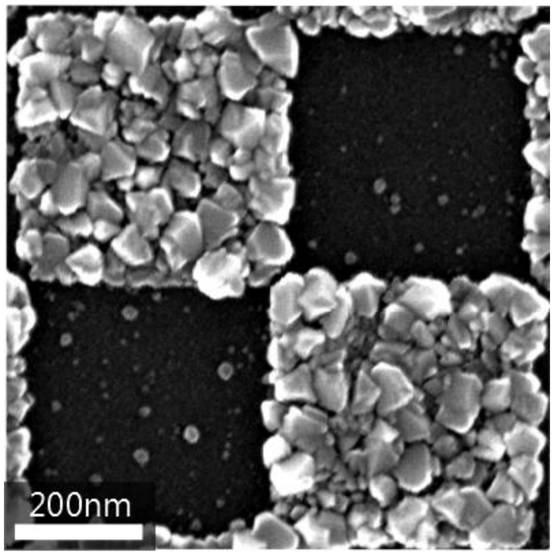
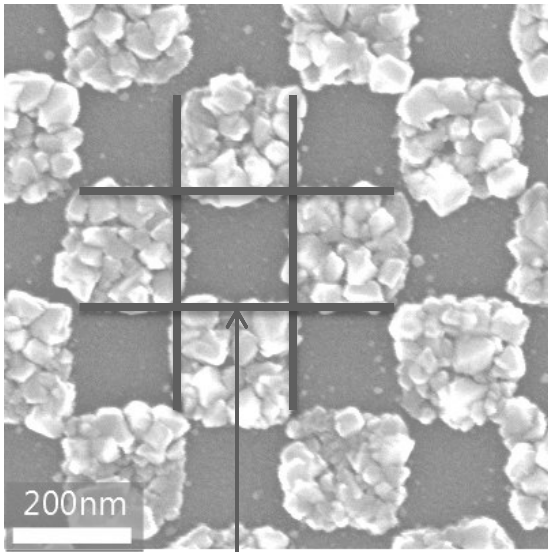


chessboard ▪ 800nm



chessboard ▪ 400nm



200nm patterning demonstrated,
Grain size of the deposit determines the sidewall sharpness

Surface Kinetics Analysis of CVD and ALD

Team involved: Michael Reinke, Evgeniy Ponomarev, Yury Kuzminykh, Patrik Hoffmann

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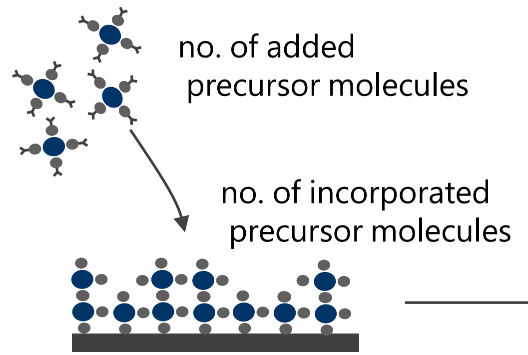
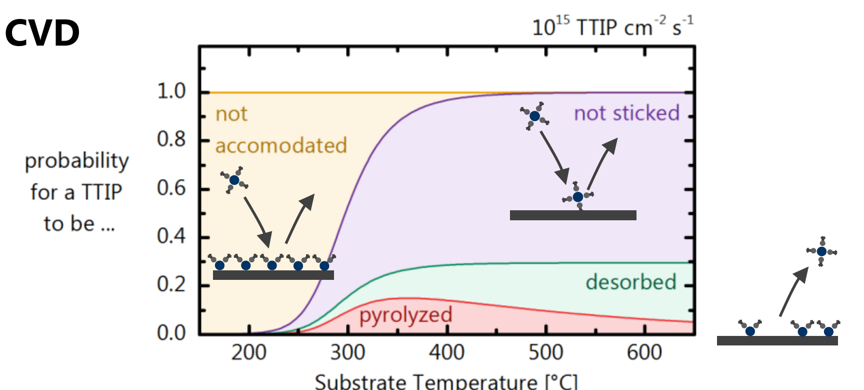
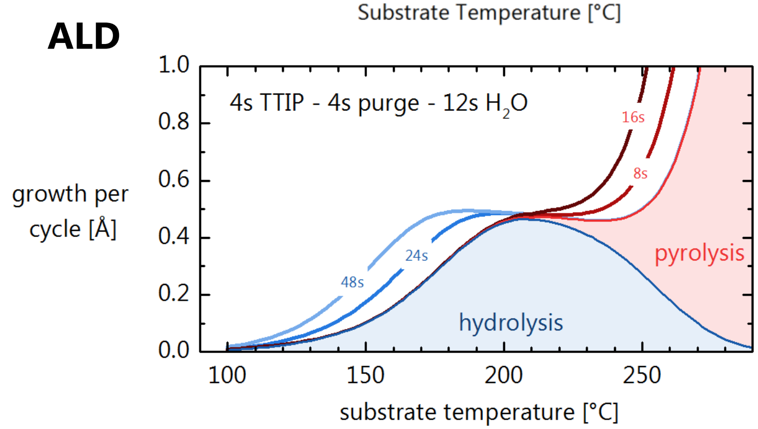


- Analysis of surface kinetics is very challenging in conventional CVD and ALD techniques

- HV-CVD allows precise control of precursor flux to the substrate; subsequent analysis reveals reaction probabilities

- Surface Kinetic parameters (activation energies) relevant for CVD and ALD can be extracted using a mathematical model to describe the deposition process





Conclusions

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Selective growth is back !

SAM’s are rediscovered

0 nucleation sites remains a challenge

No particle, no adatom, no defect allowed !!