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Area-selective ALD of SiO_2 using acetylacetone as inhibitor in a three-step cycle

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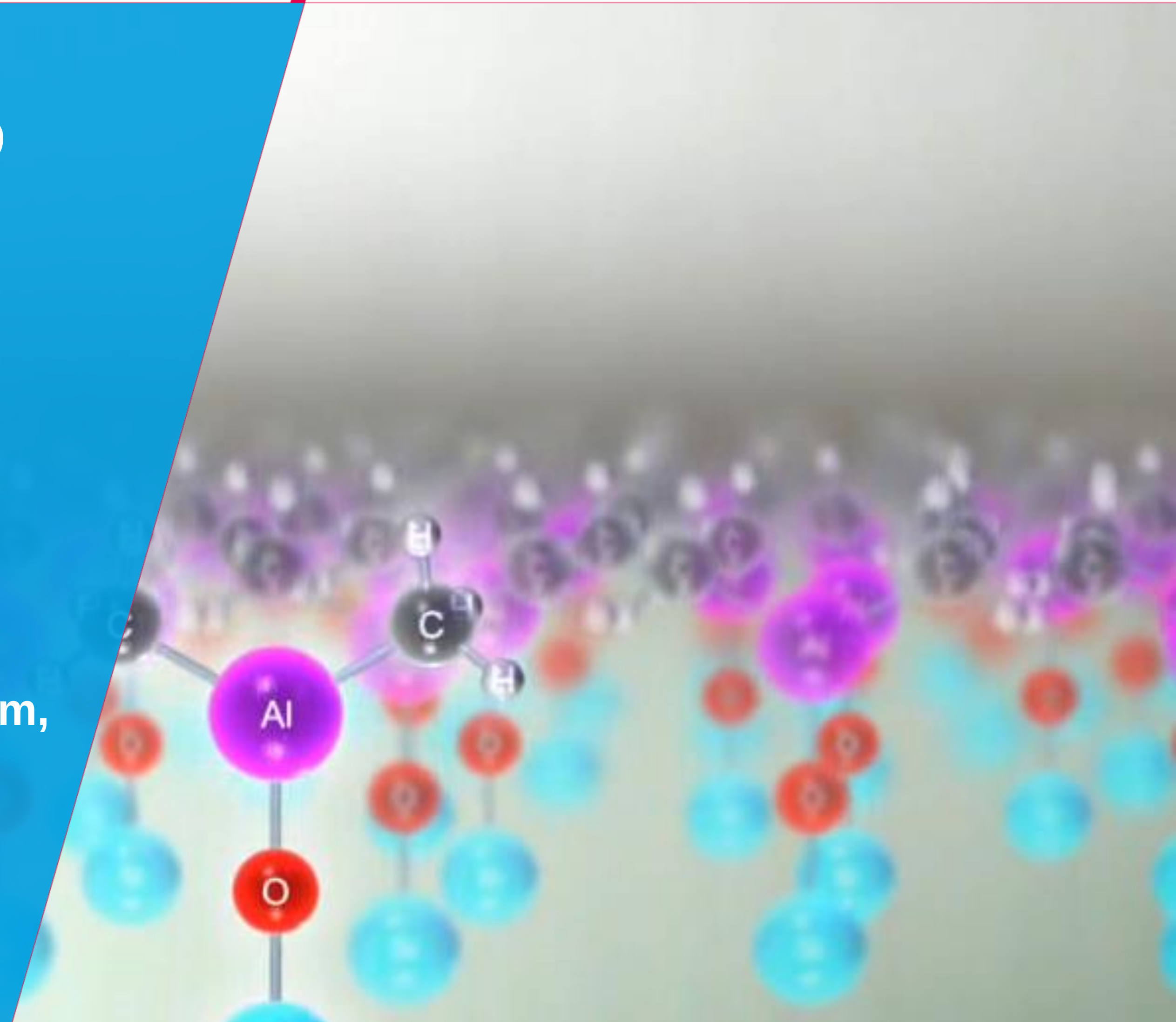
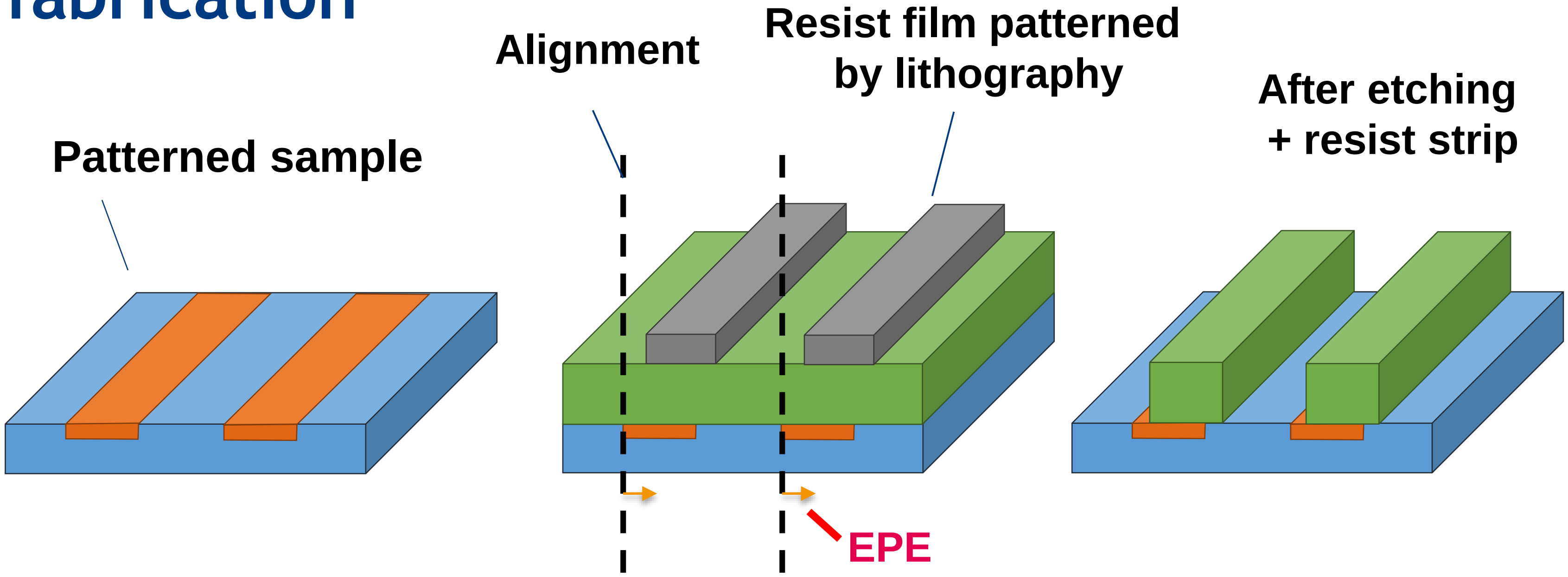


Area-selective deposition for self-aligned fabrication

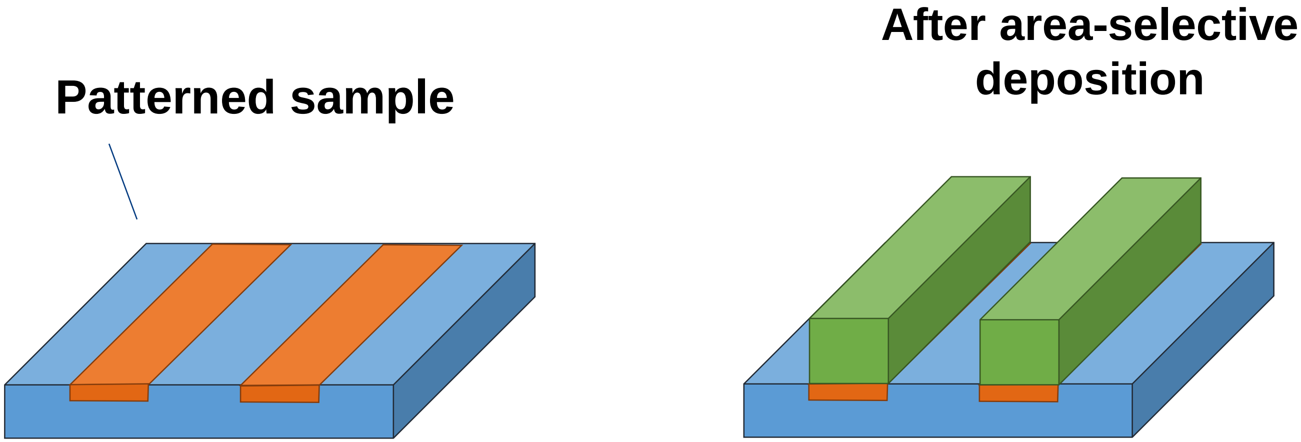


Device fabrication requires to deposit a certain material (green block) only on a certain surface (orange) while keeping clean the other surfaces

Standard approach: multi-step litho-etch litho-etch (LELE)

Challenge: the underlayer CD keep shrinking, leading to edge placement error (EPE)

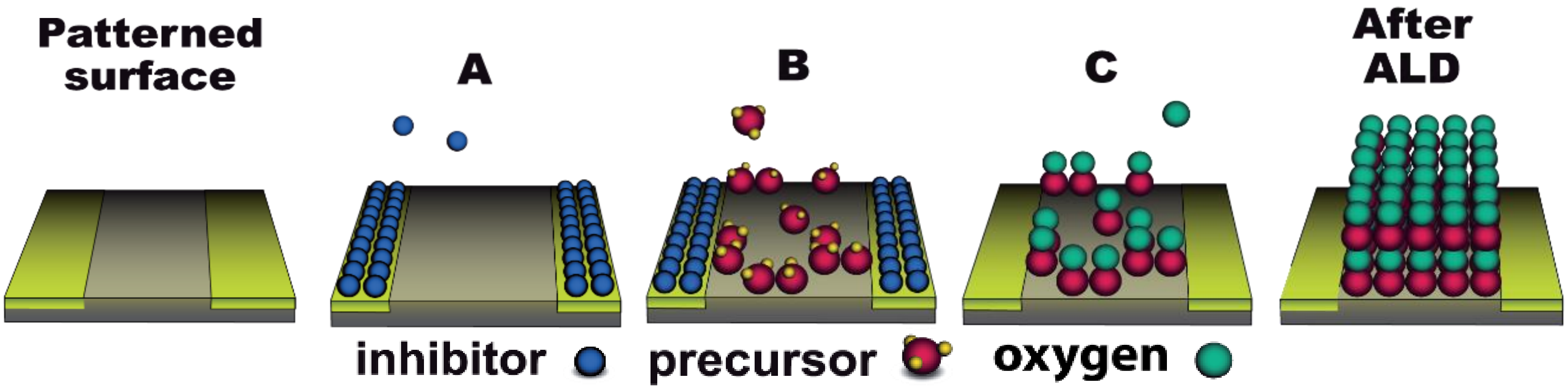
Area-selective deposition for self-aligned fabrication



Solution: Area-selective deposition (bottom-up approach)

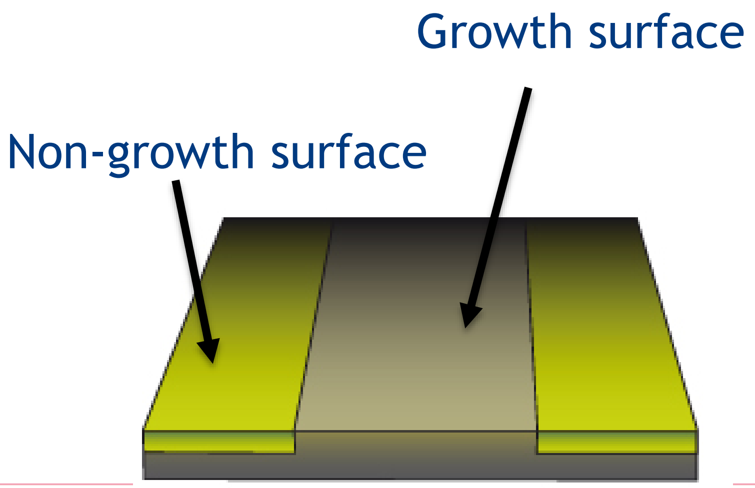
The green blocks are selectively deposited on the orange patterns ensuring perfect feature alignment

Approach: area selective ALD using molecular inhibitors in ABC processes

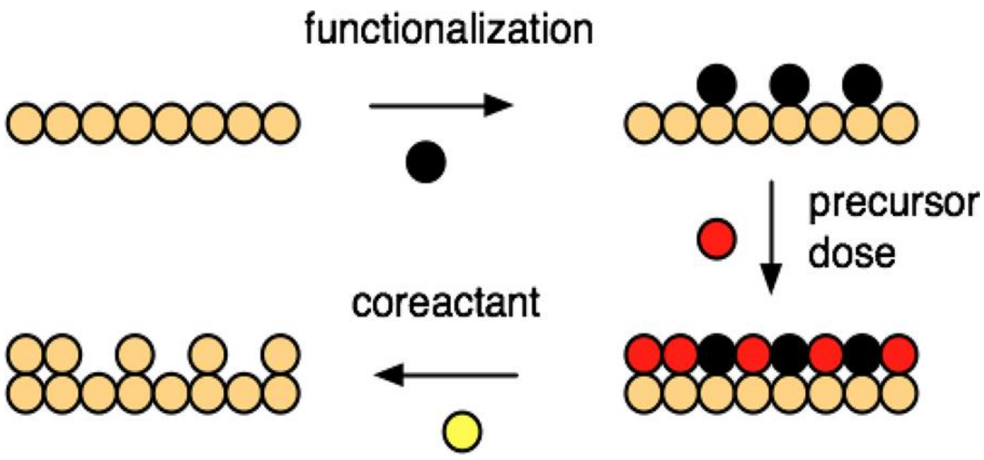


The inhibitor molecule:

- adsorbs on the non-growth surface
- blocks the adsorption of the precursor in the subsequent ALD cycle
- does not adsorb on the growth surface and the material to be deposited



ABC ALD processes with inhibitor molecules



Mechanism:
Reduction of available adsorption sites for the subsequent precursor (B) dose

Use of ABC ALD processes with
A = inhibitor molecule
has been shown to improve
the doping efficiency

Table 2. Influence of Inhibitor on the Normalized Growth Per Cycle (GPC) Values for Selected Surface-Functionalized ALD Chemistries

#	precursor	inhibitor	norm. GPC
10	TMA	CH_3COOH	0.28
11	TMA	CH_3CN	1
12	TMA	MeOH	0.40
19	DEZ	MeOH	0.33
21	DEZ	iPrOH	0.59
22	TTIP	MeOH	0.22
23	TTIP	iPrOH	0.26
24	$TiCl_4$	MeOH	0.26
25	$TiCl_4$	iPrOH	0.67

Yanguas-Gil *et al.*, *Chem. Mater.* **25**, 4849 (2013)

Outline

Novel approach for achieving area-selective ALD using a three step (ABC) process

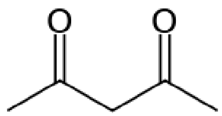
Proof of concept: area-selective ALD of SiO_2

How and why it works

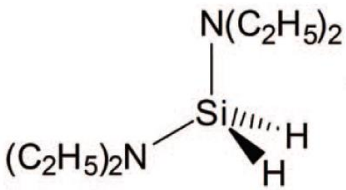
Process testing on patterned samples

Conclusions and opportunities of this approach

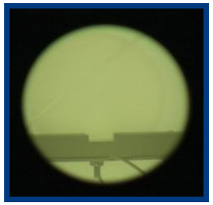
Selective growth of SiO_2



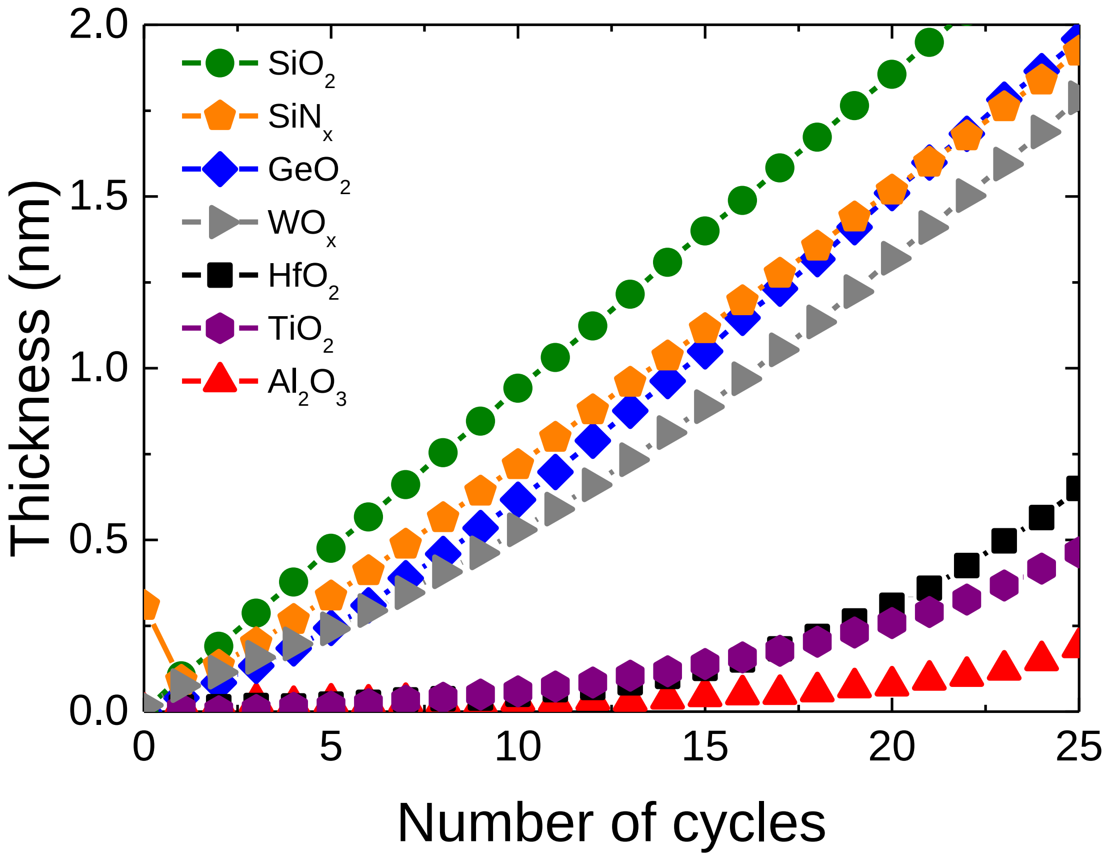
A=
Acetylacetone
(Hacac)



B =
BDEAS



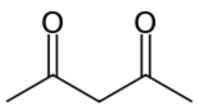
C =
O_2 plasma



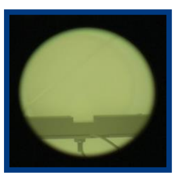
Fast nucleation on SiO_2 and Ge

Delay of 10 cycles on HfO_2 and 15 cycles on Al_2O_3

Sub-cycle ellipsometry data: case of Al_2O_3 and SiO_2



A = Hacac



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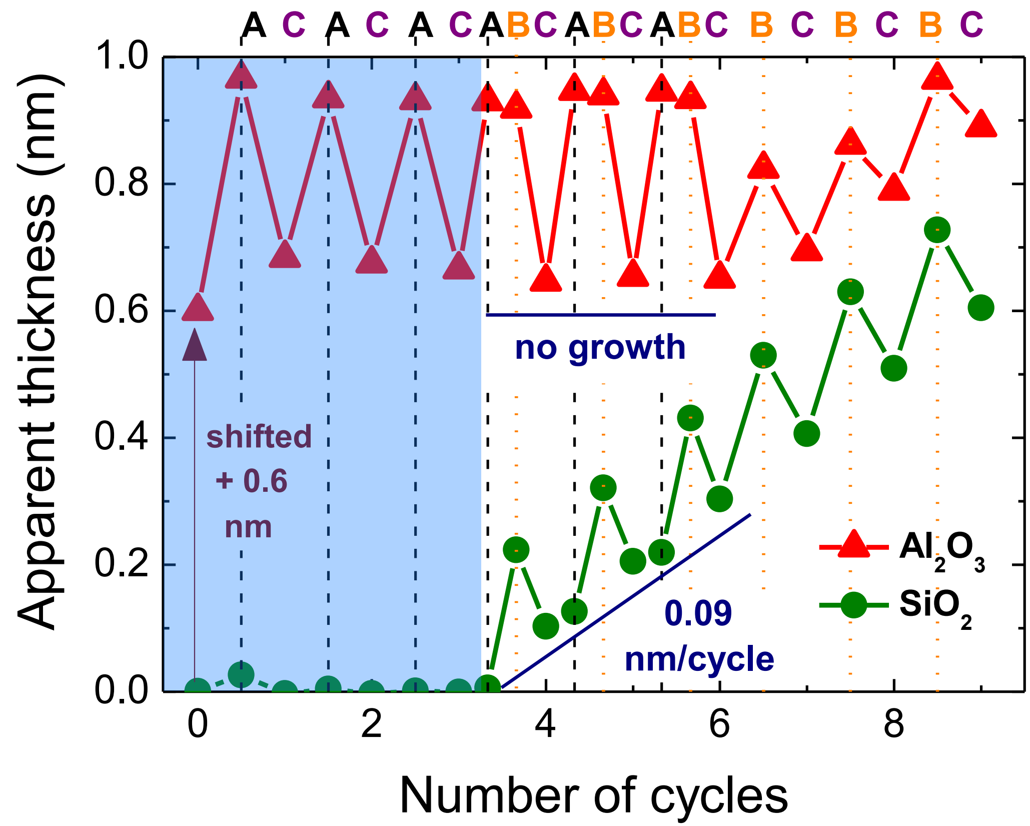
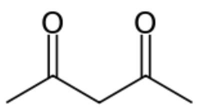


AC cycles: Selective adsorption of Hacac on Al_2O_3 and removal by O_2 plasma

ABC cycles: Adsorbed Hacac on Al_2O_3 blocks adsorption of BDEAS

BC cycles: Growth rate equal to ABC cycles on SiO_2

Sub-cycle ellipsometry data: case of Al_2O_3 and SiO_2



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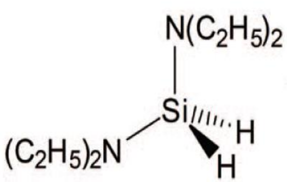

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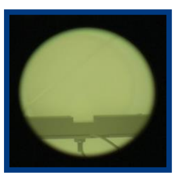

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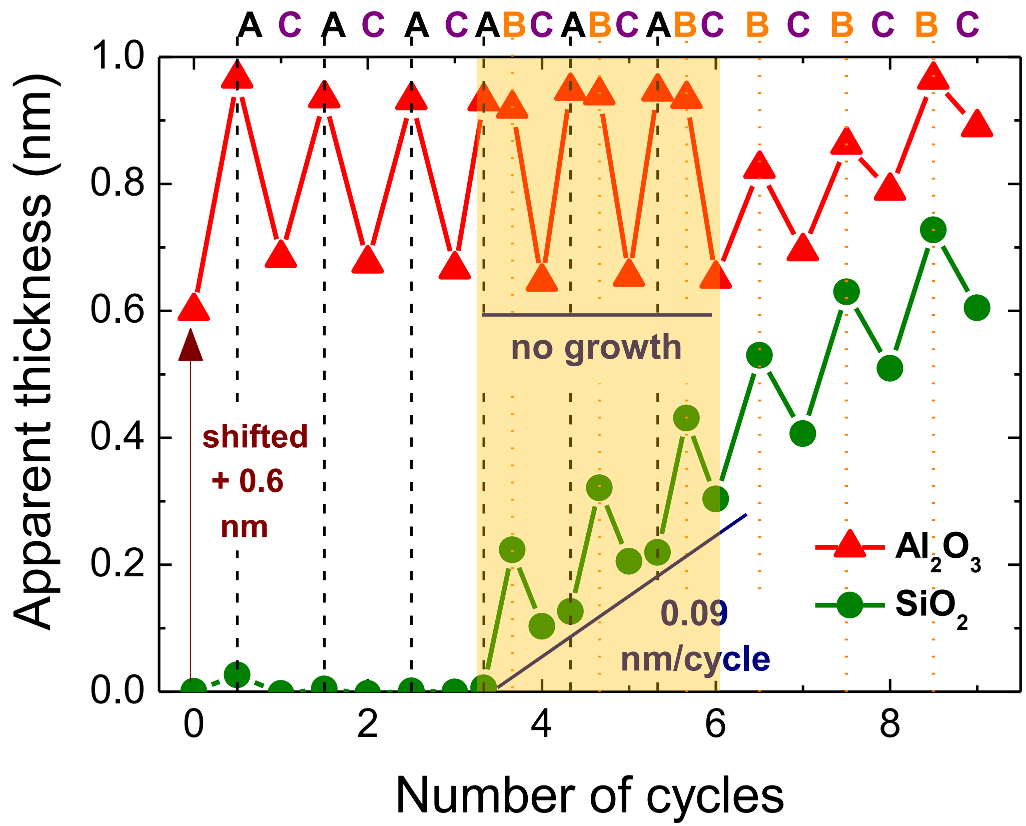

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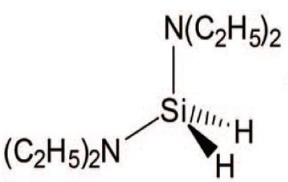

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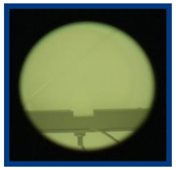

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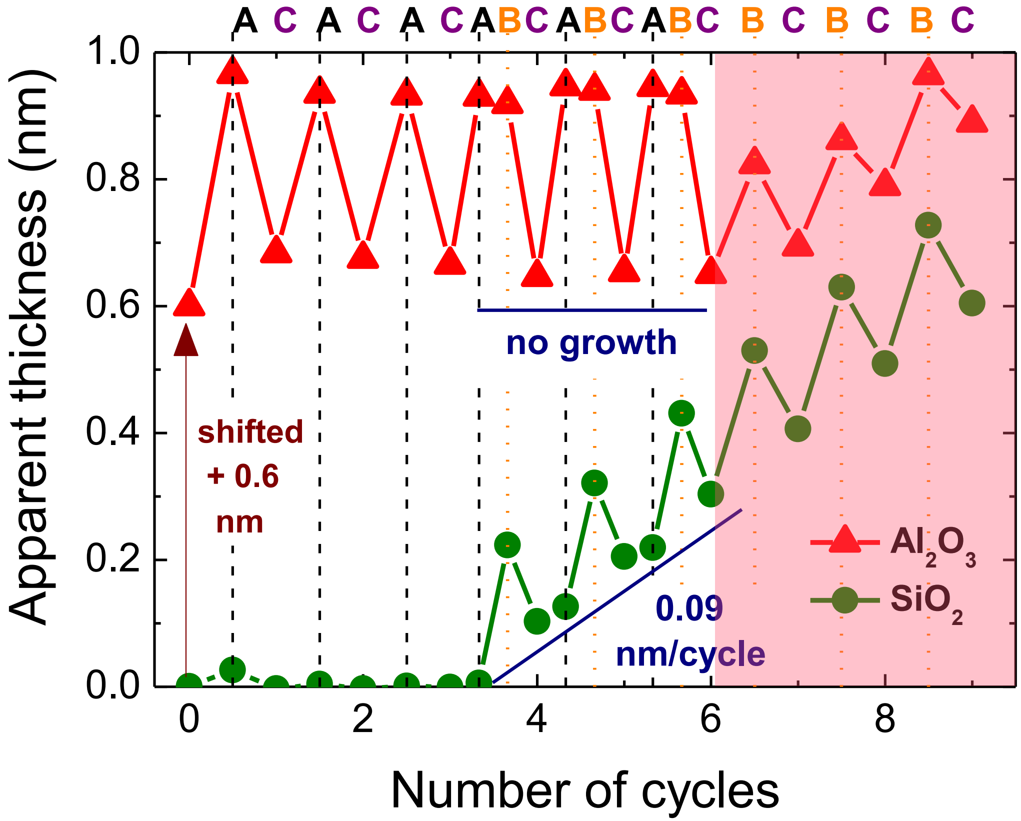

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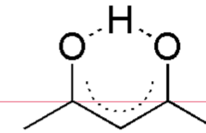
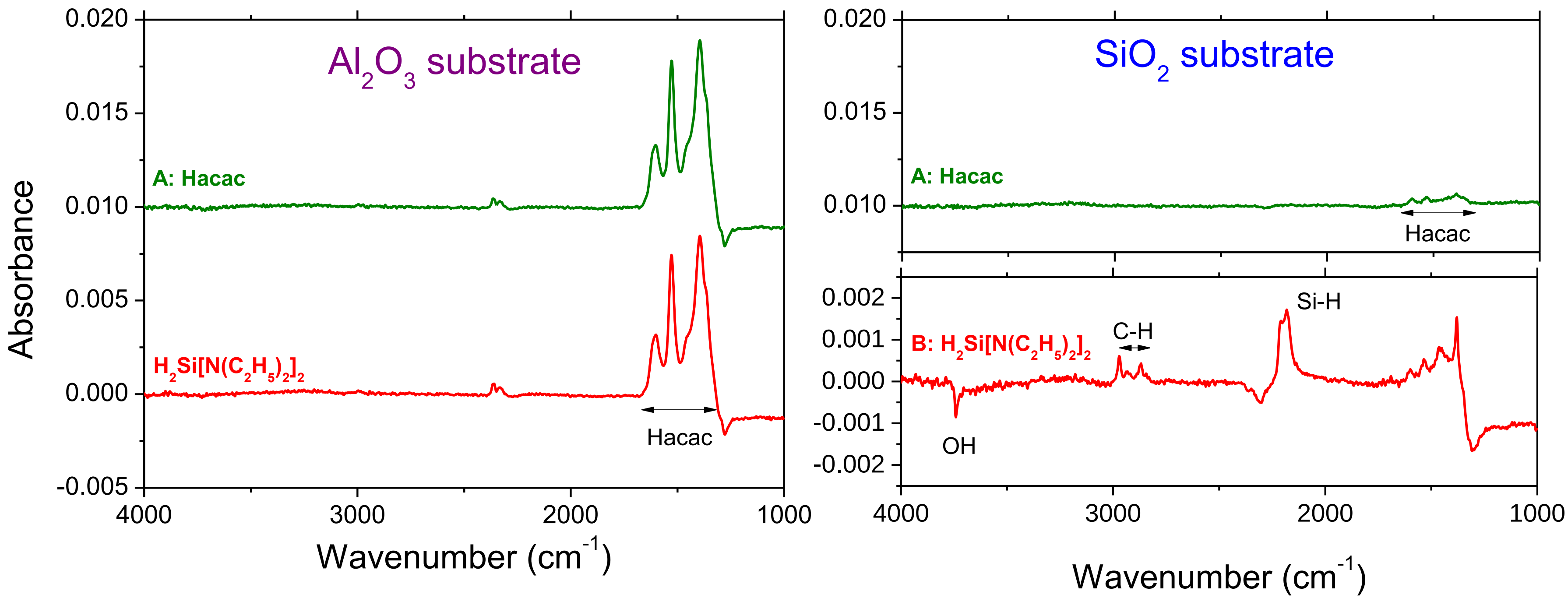
In-situ Fourier transformed Infrared Spectroscopy





Hacac adsorbs on Al_2O_3

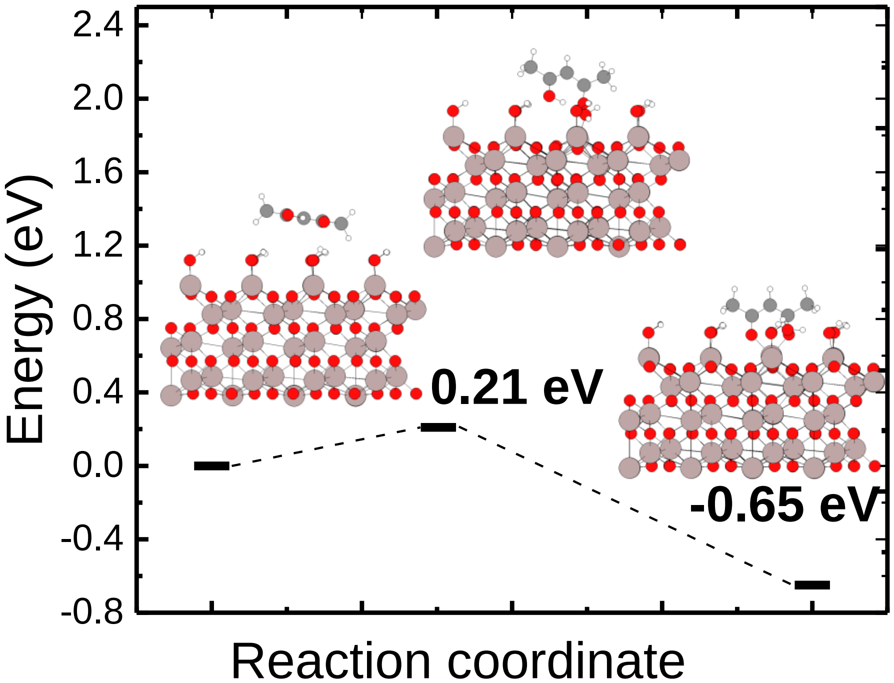
No detectable adsorption of BDEAS on Al_2O_3 grafted with Hacac

Almost no adsorption of Hacac on SiO_2

adsorption of BDEAS on SiO_2 after Hacac dose still possible

Density functional theory calculations

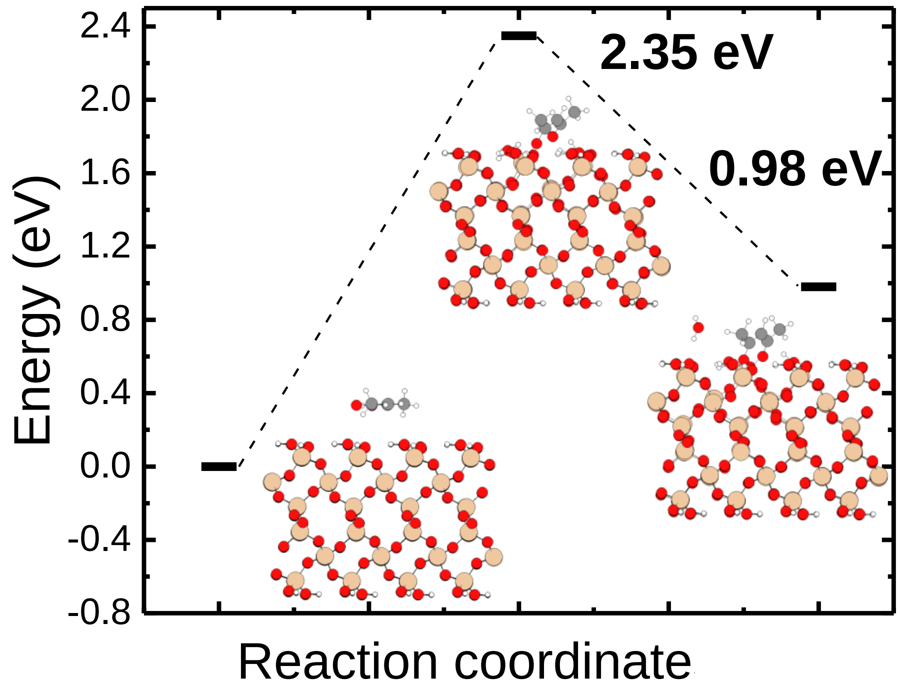
Hacac adorption on Al_2O_3



Low kinetic barrier

Thermodynamically favourable

Hacac adorption on SiO_2



High kinetic barrier
→Kinetically hindered
Thermodynamically unfavourable

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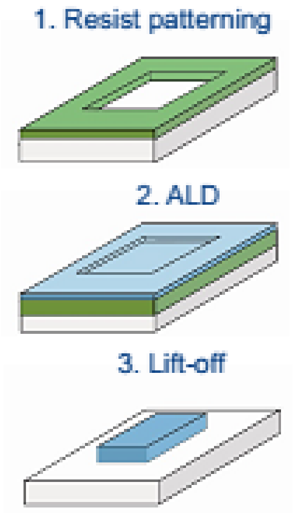
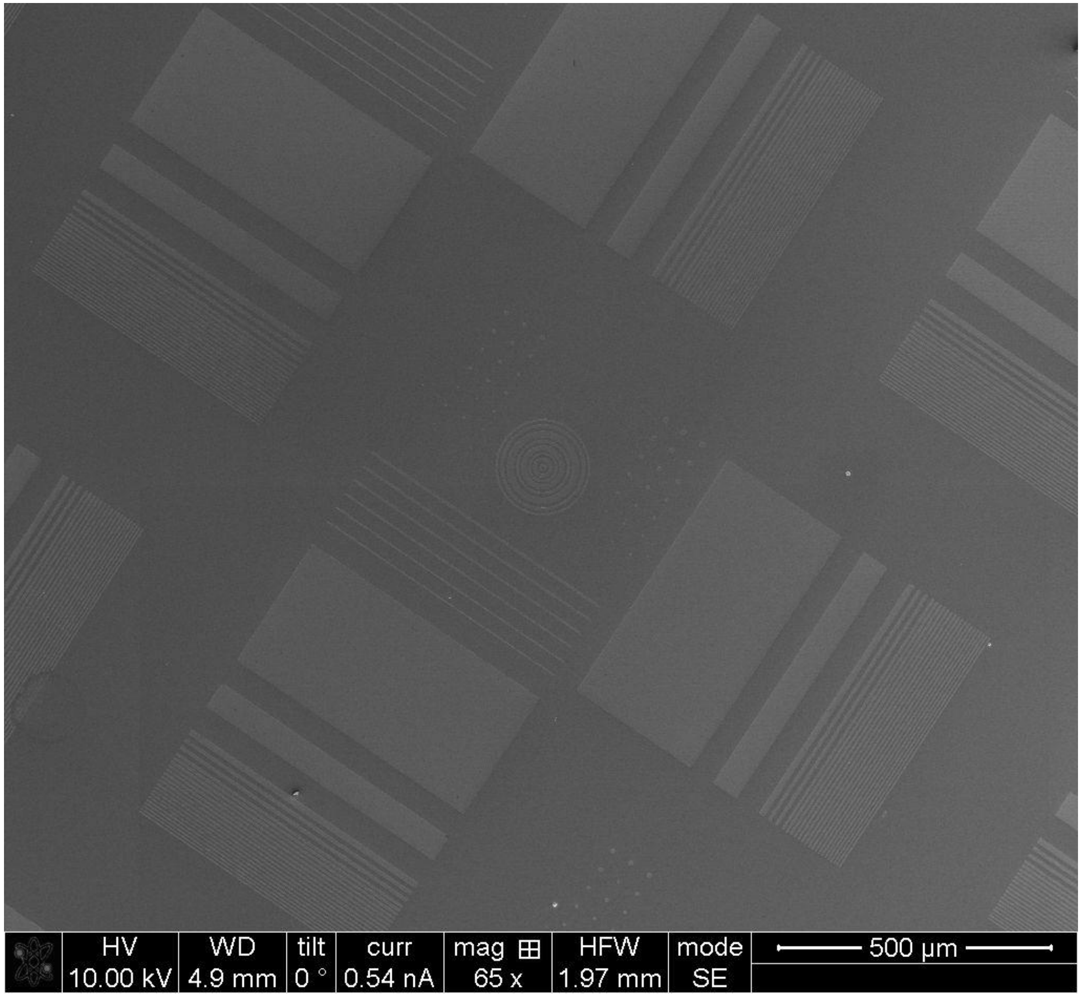
TOF-SIMS on Al_2O_3/GeO_2 patterned

Lift-off

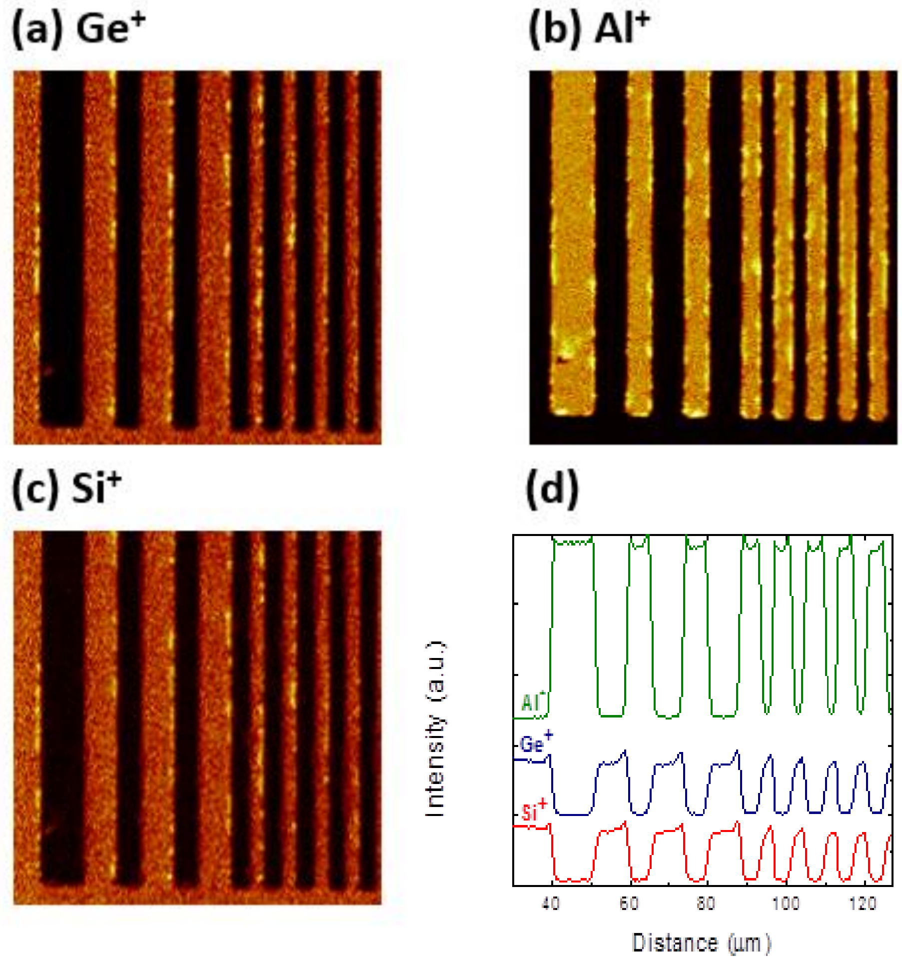




TOF-SIMS on Al_2O_3/GeO_2 patterned

Using 12 cycles (ABC) AS-ALD SiO_2 ~1 nm thick

Complementarity of Al^+ and Si^+ signals implies that SiO_2 was deposited on GeO_2 while almost no deposition occurred on Al_2O_3



Conclusions

Novel ABC AS-ALD for SiO_2 exploiting selective adsorption of inhibitor molecules

A unique feature of this new approach is that it distinguishes between different oxide surfaces (e.g. GeO_2/SiO_2 versus $Al_2O_3/HfO_2/TiO_2$)

Moreover, in contrast to most other AS-ALD approaches, it is compatible with plasma-assisted or ozone-based ALD

Can open up new application opportunities for AS-ALD

It is expected that the approach can be extended to other materials, and potentially allows for tuning the selectivity by selecting opportune inhibitor molecules

Thank you for your kind attention