Atomic Layer Deposition (ALD)

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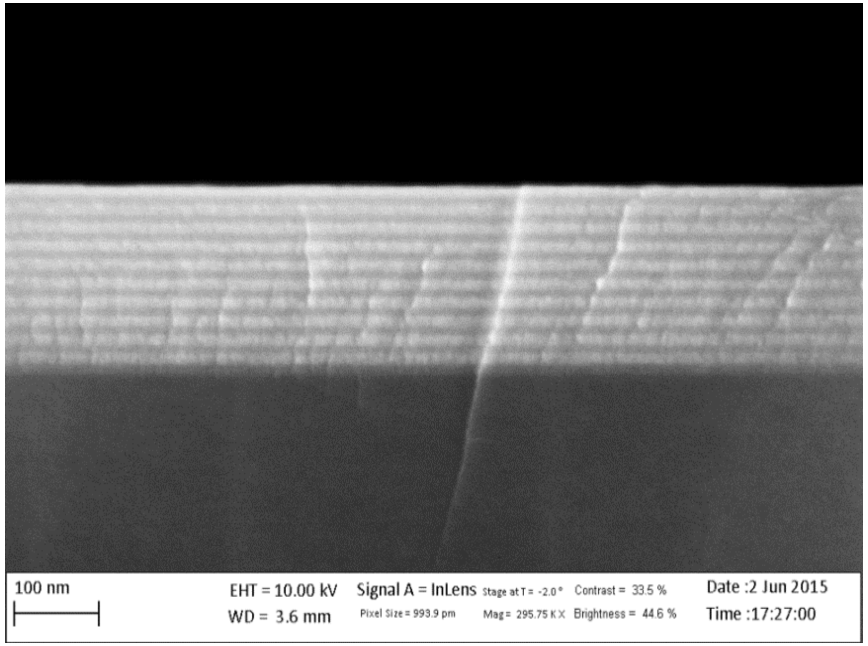
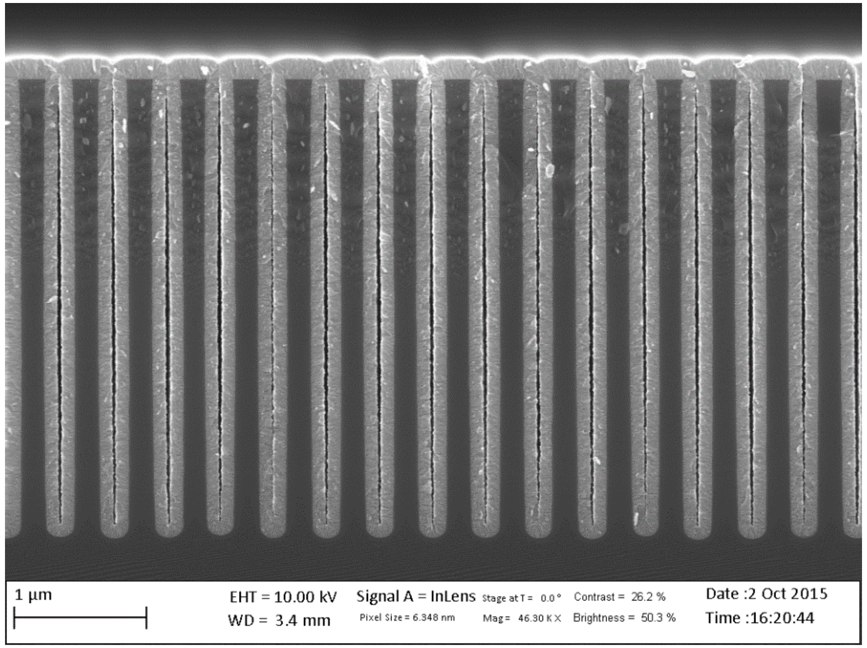
DTU Nanolab

NNUM May 2019





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What is ALD (Atomic Layer Deposition)?

ALD is a subclass of chemical vapour deposition (CVD) thin film coating techniques

ALD depositions can be done on almost all kinds of samples, including samples with low melting point and complex 3D structures

With ALD ultra thin and uniform layers are deposited monolayer by monolayer everywhere on the sample surface

Two different kinds of ALD:

1. Thermal ALD – Thermally driven reaction
2. Plasma enhanced ALD (PEALD) – Plasma enhanced reaction

ALD was developed in 1974 in Finland by Dr. Tuomo Suntola

ALD – Deposition materials

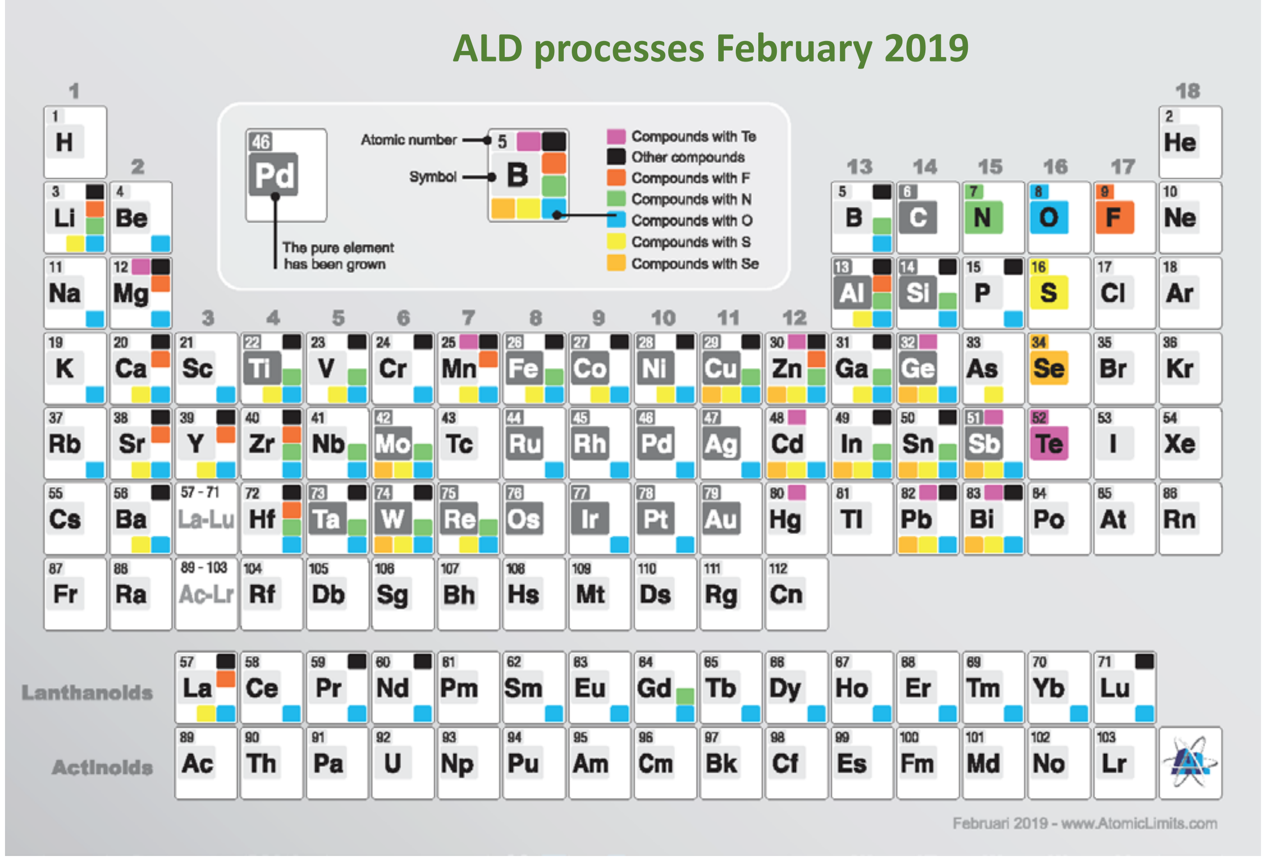
Very many different materials can be deposited by ALD

Materials typically deposited by ALD:

- **Oxides:** Al_2O_3, TiO_2, HfO_2, SiO_2, Ta_2O_5, ZnO, ...
- **Nitrides:** AlN, TiN, HfN, TaN, ...
- **Fluorides**: AlF_3, MgF_2 , ...
- **Sulfides:** ZnS, MoS_2, ...
- **Metals:** Pt, Ni, Ru, ...

Materials that can be deposited at DTU Nanolab:

- **Oxides:** Al_2O_3, TiO_2, HfO_2, SiO_2, ZnO, AZO (Al-doped ZnO)
- **Nitrides:** AlN, TiN



https://www.atomiclimits.com/2019/01/28/overview-of-all-materials-prepared-by-atomic-layer-deposition-ald-an-up-to-date-and-colorful-periodic-table-to-download/

Nordic Nanolab Network

ALD (Atomic Layer Deposition) in general and thermal ALD

ALD - Precursors

The chemicals used for ALD depositions are called precursors

- Liquids, solids or gases for thermal ALD
- Percursor bottles can be heated or cooled if necessary
- Reactive species can also be generated by a plasma (for PEALD)

Normally two precursors (A and B) are used for a deposition

Example*: Thermal ALD deposition of* Al_2O_3

Precursor A: TMA (trimethylaluminium)
Precursor B: Water

Overall ALD reaction:

$$2\,Al(CH_3)_3 + 3\,H_2O \xrightarrow{\textbf{Heat}} Al_2O_3 + 3\,CH_4$$

TMA — **Water** — **Aluminium oxide** — **Methane**

ALD - Reaction

ALD reactions take places in cycles

Reaction for one ALD reaction cycle:

1. Precursor A pulse
Precursor A adsorbs on and reacts with the sample surface, until all available sites are occupied

2. Inert gas purge
Remaining unreacted precursor together with by-products are purged away

3. Precursor B pulse
Precursor B reacts with precursor A on the sample surface, and the reaction leads to the desired deposition material

4. Inert gas purge
Remaining unreacted precursor together with by-products are purged away

One monolayer is deposited per cycle

The cycle is repeated *(A pulse, purge, B pulse, purge, A pulse…)* until a uniform layer with a decided thickness is deposited

Typical deposition rate ~ 0.5-1 Å/cycle

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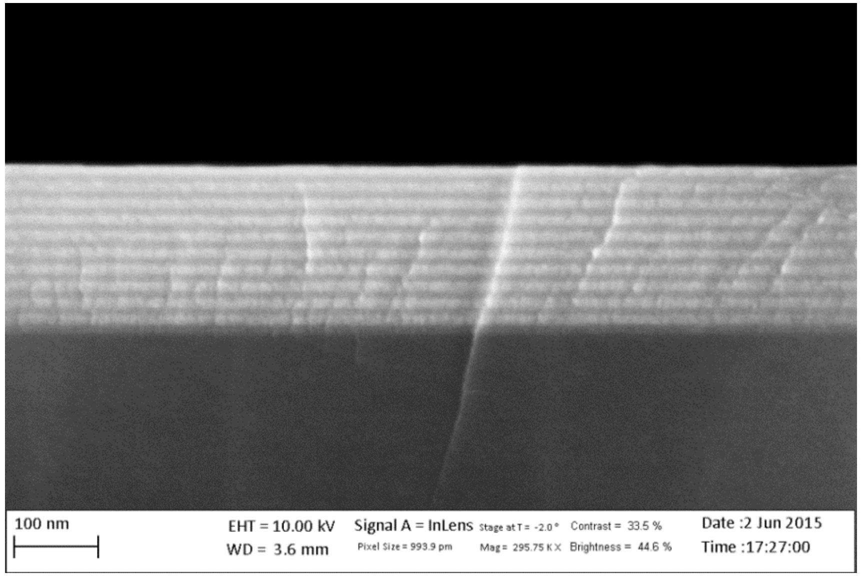
ALD - Reaction

Properties of the ALD reaction:

- **No gas-phase reactions**
  - Precursors are introduced in the ALD chamber sequentially and should never be present in the chamber simultaneously
  - All reactions takes place on the sample surface – Never in the gas phase

- **Self-limiting reaction**
  - One monolayer is deposited per ALD cycle. No further reactions can take place, once the sample surface is completely saturated

- **Sequential deposition steps**
  - The number of cycles controls the thickness of the deposited layer



Si sample with multilayers of Al_2O_3 and TiO_2

Physical Review Letters 115, 177402 (2015)

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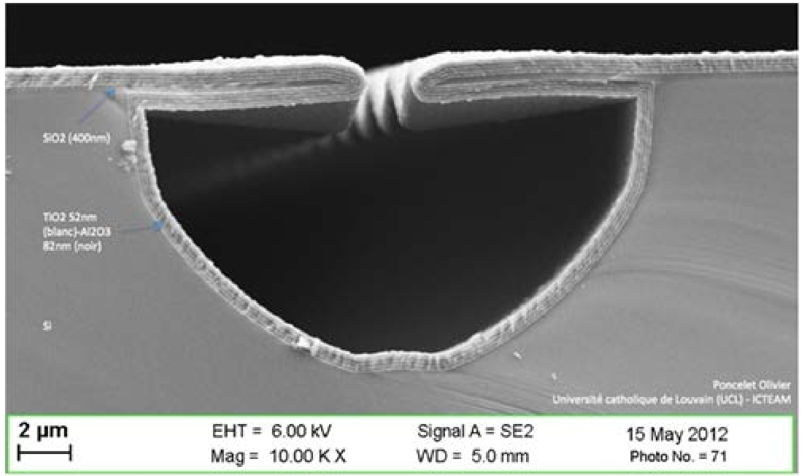
ALD reaction - Deposition on high aspect ratio structures

With ALD, uniform layers can be deposited everywhere on the surface of almost all structures, e.g.

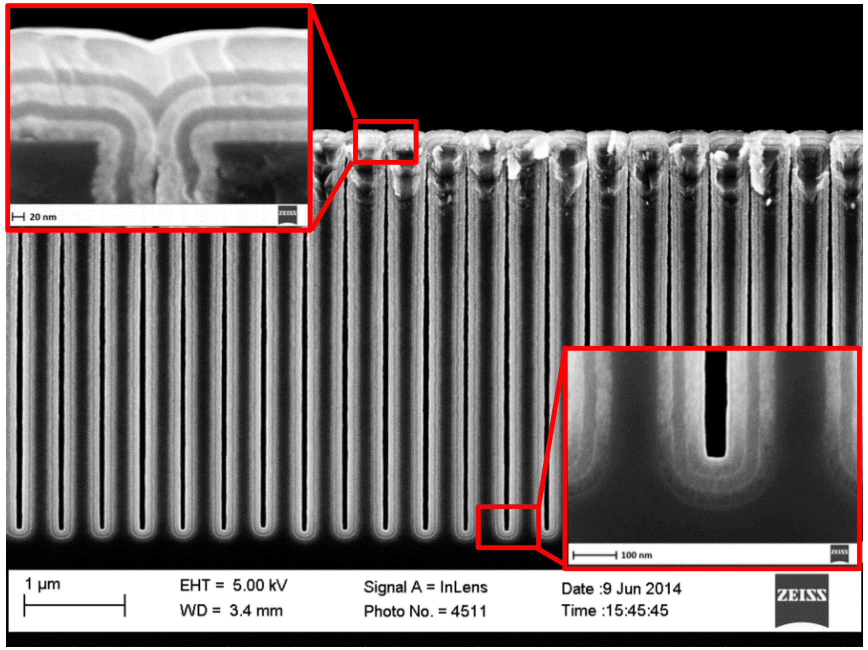
- Complex 3D objects
- Structures with high aspect ratio
- Porous materials

Thus, the uniformity and step is very good compared to other CVD deposition techniques



Al_2O_3 and TiO_2 layers deposited in a 3D cavity

http://www.cambridgenanotechald.com/applications/3d-nanofabrication.shtml



Al_2O_3 and TiO_2 layers deposited on high aspect ratio trenches

Trench depth ≈ 4 µm, width ≈ 200 nm

ALD – Deposition time

The cycle time for the ALD reaction depends on:

- The surface reaction behaviour
- The sample surface structure – high aspect ratio structures requires long purge times

Example - How long time does it take to deposit 100 nm of Al_2O_3?

Deposition rate at 200°C: 0.097 nm/cycle

Using a standard recipe for deposition of Al_2O_3:

	TMA	H_2O
Pulse time	0.1 s	0.1 s
N_2 purge time	3.0 s	4.0 s

Total cycle time: 7.2 s

Deposition time for 100 nm Al_2O_3: $\frac{100\text{ nm}}{0.097\text{ nm/cycle}} = 1031\text{ cycles}$

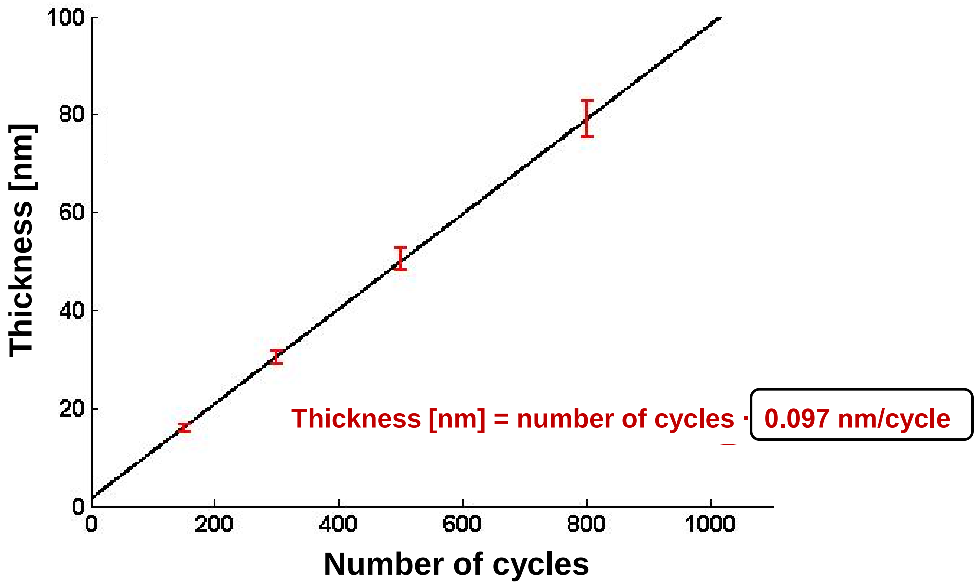
$$1031\text{ cycles} \cdot 7.2\frac{\text{s}}{\text{cycle}} = 7423\text{ s} = 124\text{ min} \approx \boxed{2\text{ h}}$$

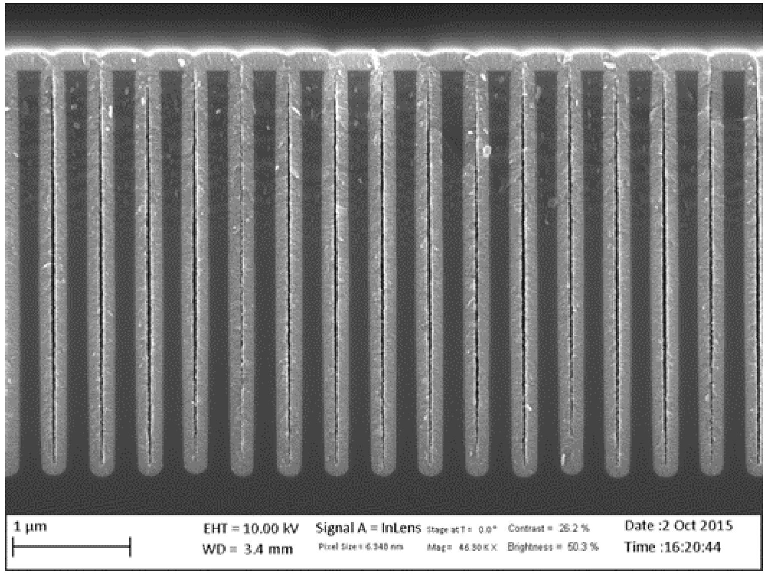
Using the recipe for deposition of Al_2O_3 on high aspect ratio structures:

Total cycle time: 41.4 s

Deposition time for 100 nm Al_2O_3: $1031\text{ cycles} \cdot 41.4\frac{\text{s}}{\text{cycle}} = 42683\text{ s} = 711\text{ min} \approx \boxed{12\text{ h}}$

Thickness as function of number of cycles for Al_2O_3 deposited at 200 ˚C



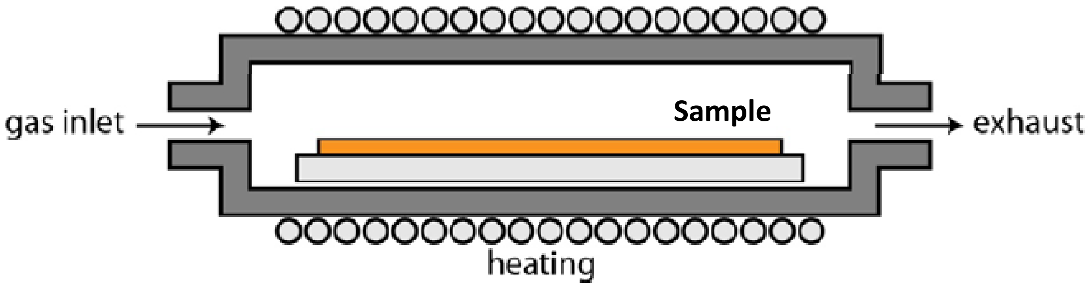


Thermal ALD – Equipment overview

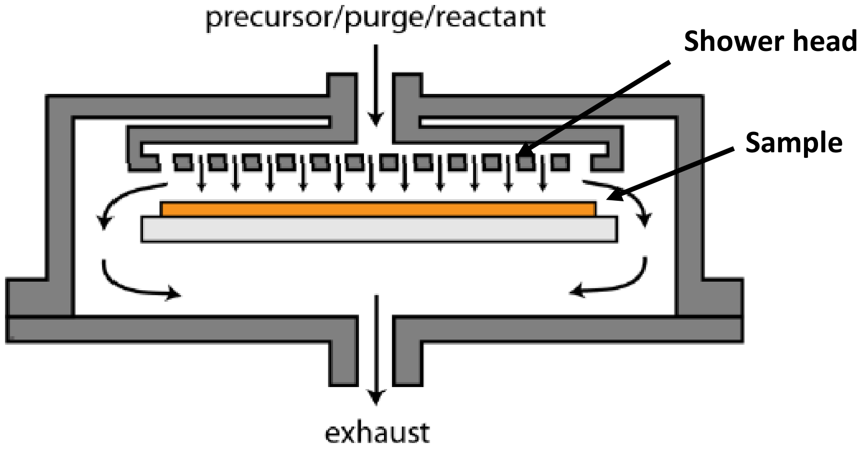
ALD depositions takes place in an ALD reactor chamber

- Hot wall ALD: The temperature is the same everywhere in the chamber
- Cold wall ALD: Samples are lying on a heated plate with higher temperature than the chamber walls

Flow type reactor



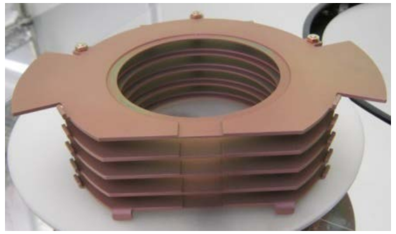
Shower head reactor



https://www.vacuum-uk.org/pdfs/vs4/ALD_Kessels.pdf

Thermal ALD – Equipment overview (ALD the DTU Nanolab)

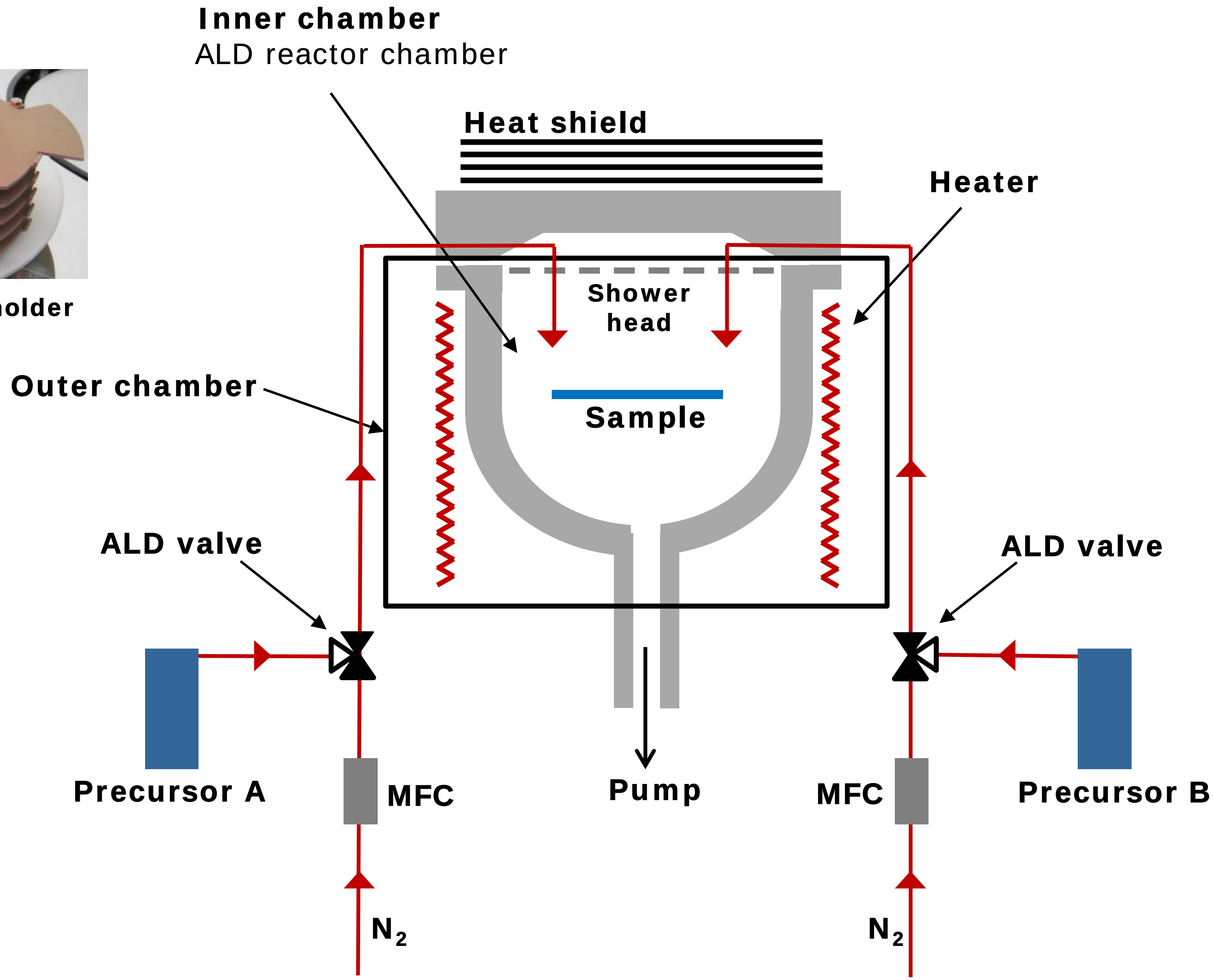
Sample(s):
- Depositions can be done on one or more samples/wafers at a time


Mini batch sample holder

Temperature control:
- The ALDs at DTU Nanolab are hot wall ALDs
- There are heaters in between the inner chamber (the ALD reactor chamber) and the outer chamber

Pressure control:
- ALD depositions take place under vacuum
  Pressure ~ 1 mbar = 100 Pa

Precursor and purge control:
- The precursor pulse time is controlled by ALD valves having a very short reaction time (0.1 s)
- Precursor lines are constantly purged with N_2.
  MFCs (mass flow controllers) control the N_2 flow



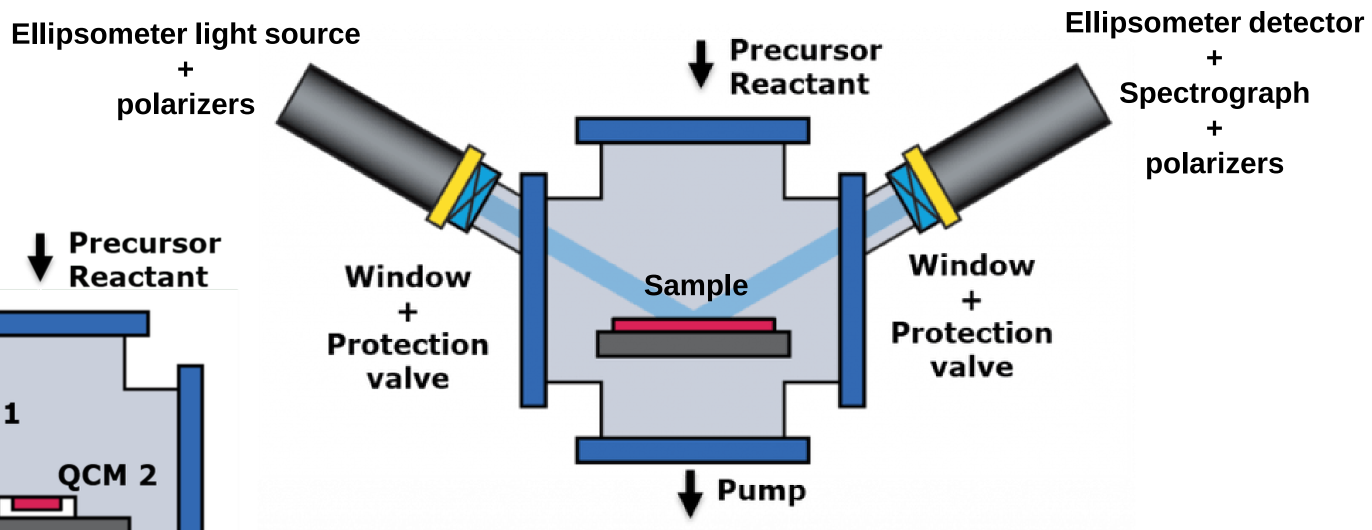
Thermal ALD – System overview (in-situ measurements)

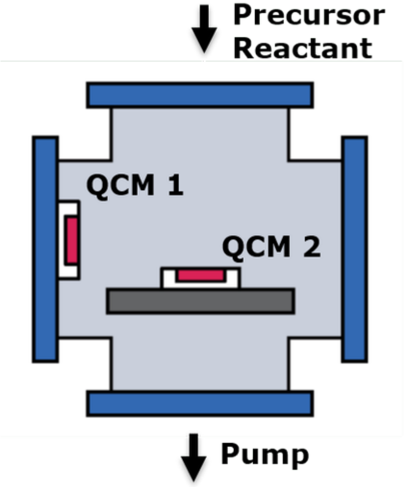
Ellipsometry:

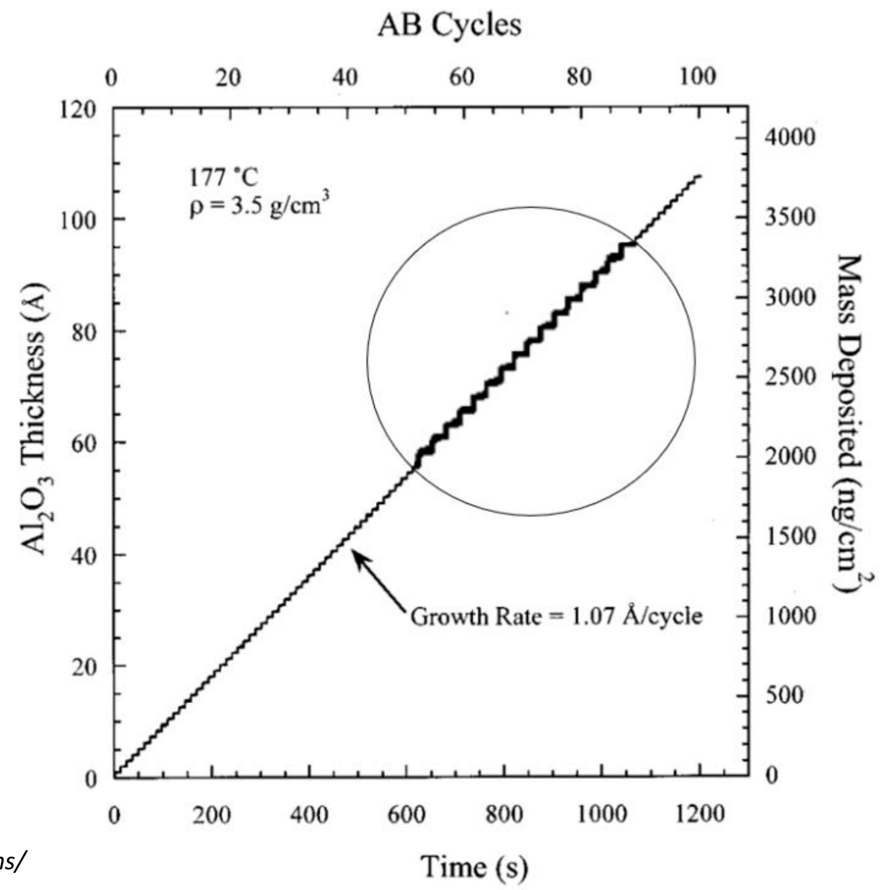
- Measures the change in polarization of a light beam that has been reflected from the sample for a range of wavelengths
- The thickness, refractive index and other optical parameters for the deposited material can be found

Quartz crystal microbalance (QCM):

- Measures very small changes in mass by probing the resonance frequency of a quartz crystal resonator being covered by the deposited material







https://www.atomiclimits.com/2018/07/28/in-situ-studies-of-ald-processes-reaction-mechanisms/

ALD – Temperature window

Ideal ALD depositions take place within a certain temperature range called the ”ALD temperature window”

The temperature window is very process dependent

Example: *Thermal ALD deposition of Al_2O_3*

Recap from earlier:

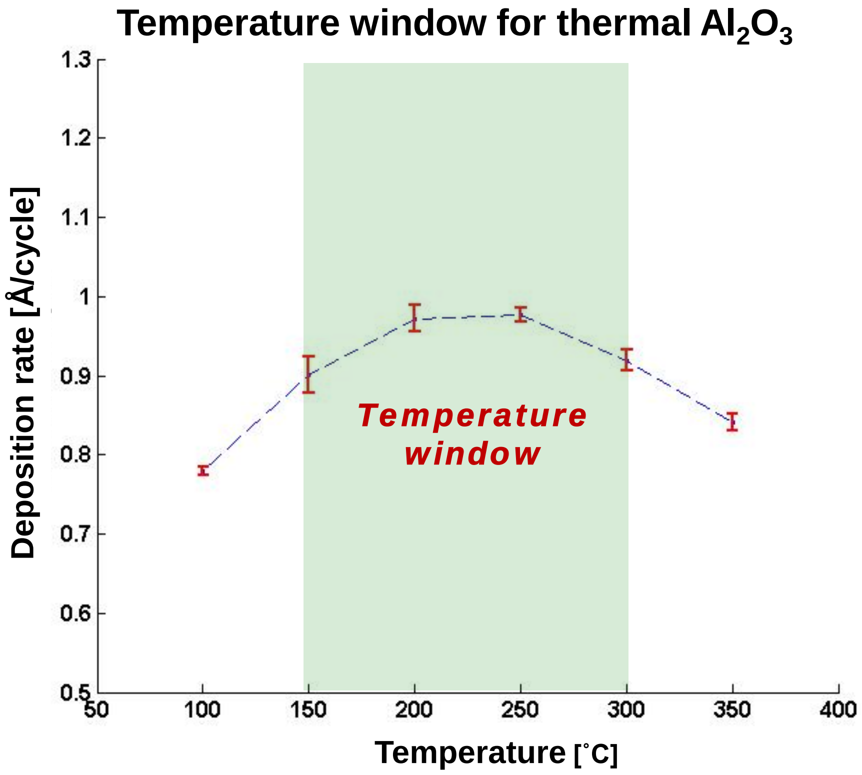
Overall ALD reaction:

$$2\,Al(CH_3)_3 + 3\,H_2O \xrightarrow{\textbf{Heat}} Al_2O_3 + 3\,CH_4$$

TMA (trimethylaluminium) — **Water** — **Aluminium oxide** — **Methane**

Temperature window: 150°C – 300°C

Temperature < 150°C: Unreacted TMA
Temperature > 300°C: TMA decomposes



ALD – Temperature window

Within the temperature window, the ALD reaction is:

- Self-limiting – One monolayer is deposited per cycle
- Complete
- Irreversible

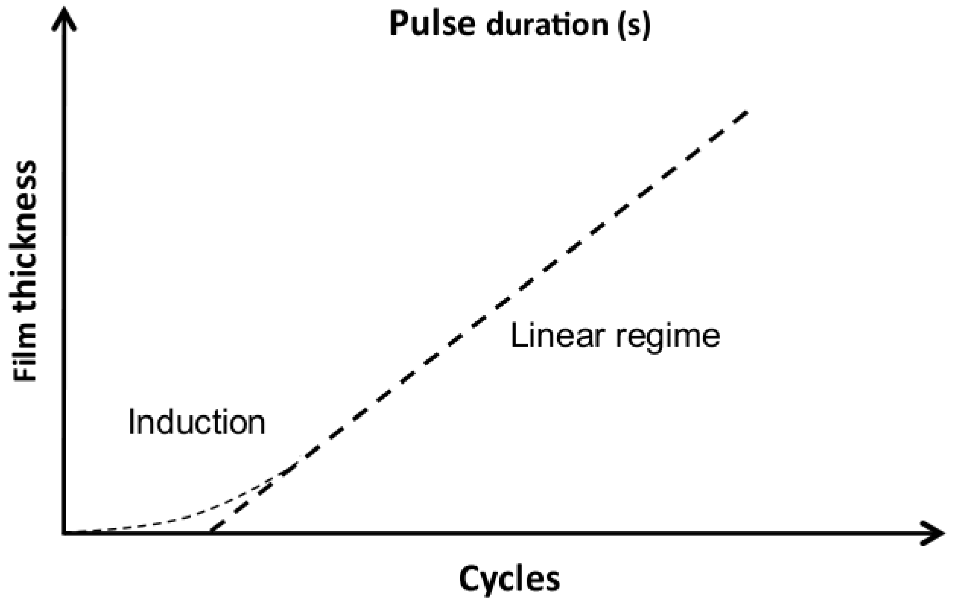
Outside the temperature window, the deposition rate is uncontrolled (too high or too low), or nothing is deposited

- Condensation:
  - *Precursors condense on the sample surface*
- Decomposition
  - *Thermal decomposition of precursors on the sample surface (CVD)*
  - *The deposited material is affected by unreacted precursor molecules*
- Incomplete reaction:
  - *Too low thermal energy for a sample surface reaction*
- Desorption/evaporation:
  - *Molecules do not stay on the sample surface*

ALD - Limitations

Limitations:

- The surface has to be reactive with the precursors – Otherwise no reaction will take place
- Some monolayers have to be deposited before a closed layer is formed on the sample surface, especially if there are impurities on the surface
- The required thermal energy for the ALD reaction (thermal ALD) – deposition on the samples with low melting point not always possible
- Slow deposition rate (0.01-0.1 Å/s)
- Precursors:
  - Expensive
  - Toxic and/or flammable
  - Only space for a few (4-8) precursors on the ALD at time



Paul Chalker, University of Liverpool

PEALD (Plasma Echanced ALD)

Plasma Enhanced ALD (PEALD)

In PEALD very reactive plasma species deliver the necessary activation energy for the reaction to take place

The sample surface will be exposed to the reactive gas species in one of the pulse steps in the reaction cycle

With PEALD, typically reactive species from oxygen (O), hydrogen (H*) or nitrogen (N*) plasma replace H_2O or NH_3 in thermal ALD*

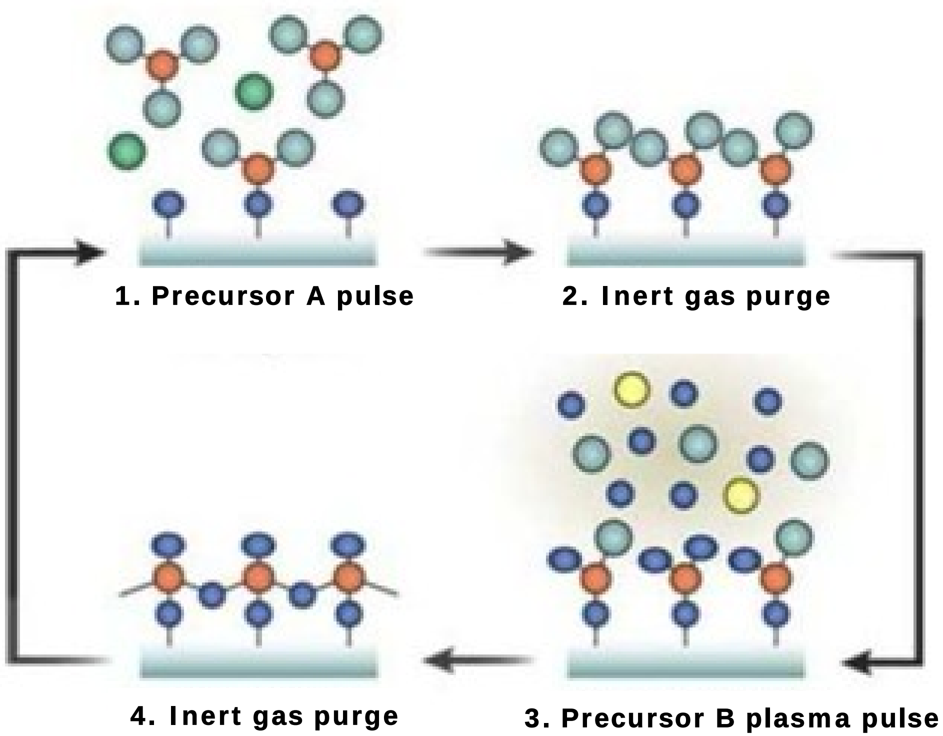
Example: *PEALD deposition of Al_2O_3*

Precursor A: TMA (trimethylaluminium)
Precursor B: Oxygen plasma

Overall ALD reaction:

$$2\,Al(CH_3)_3 + 24\,O^{*} \rightarrow Al_2O_3 + 6\,CO_2 + 9H_2O$$

TMA	Oxygen	Aluminium oxide	Carbon dioxide	Water



Aalto University, https://slideplayer.com/slide/10548116/

The sample is exposed to very reactive oxide plasma species which oxidize the surface

PEALD – Plasma generators

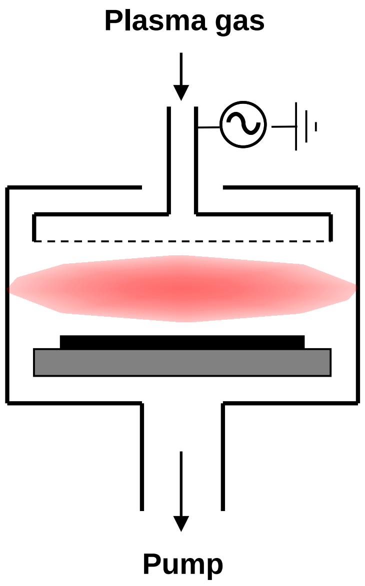
In PEALD very reactive gas species are created by a plasma generator

There are two main types of PEALD plasma generators: Direct and remote RF plasma

Direct RF plasma

The sample is directly exposed to plasma

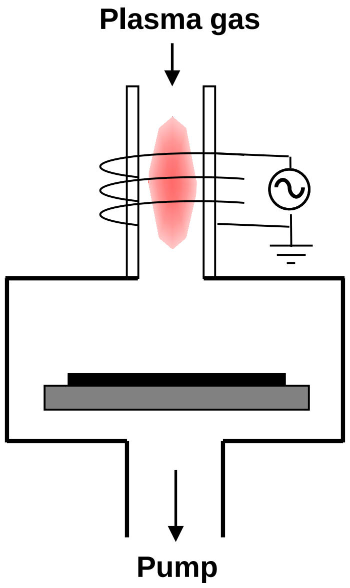
Very good plasma uniformity, but the sample surface is exposed to high energy ions (> 100 eV) ⇒ Possible sputtering



Remote RF plasma

The sample is not involved in the plasma creation

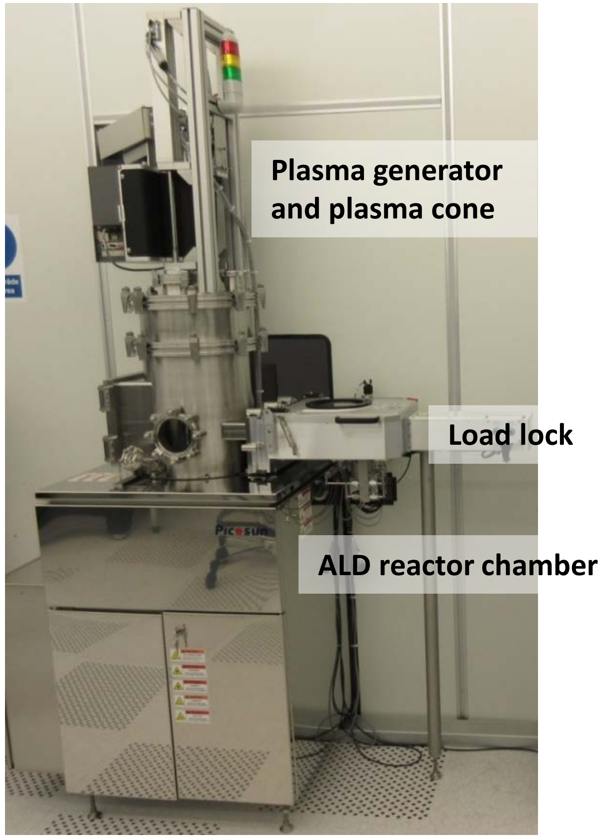
Not so good uniformity, but the sample surface is only exposed to low energy ions (< 20 eV) ⇒ Almost no sputtering



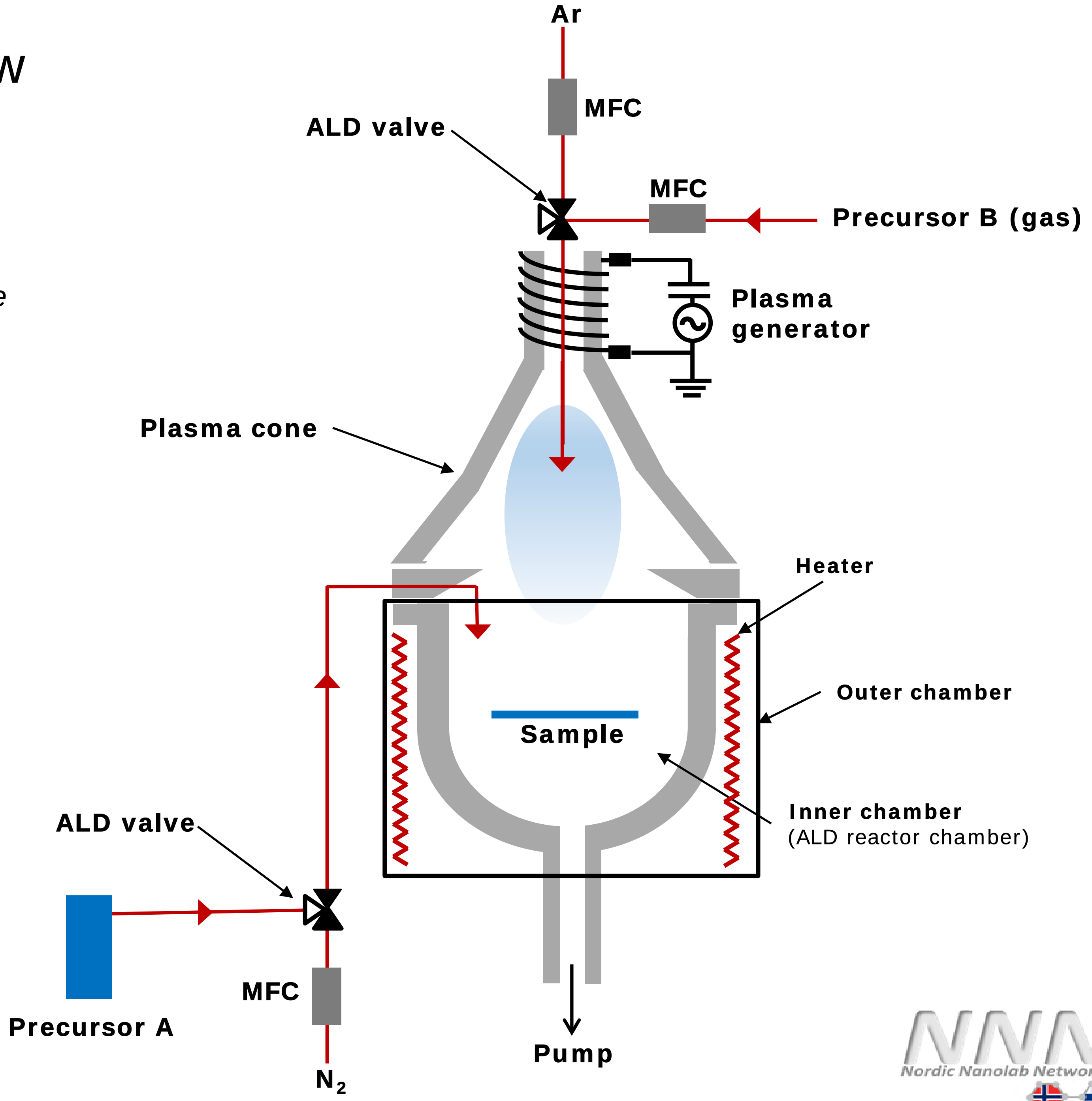
PEALD – Equipment overview (PEALD at DTU Nanolab)

Remote RF plasma

The plasma is generated in a plasma cone above the ALD reactor chamber



Picosun R200 Advanced thermal ALD and PEALD



PEALD – Advantages and limitations

PEALD advantages (compared to thermal ALD):

- Deposition of more materials
  - More precursors available
- Deposition of ”difficult” materials, e.g. nitrides and metals
- Lower deposition temperature (down to room temperature) – The reactive plasma species deliver the necessary activation energy for the reaction to take place
- Higher deposition rates per cycle
- Better control of film stoichiometry
- Improved materials properties
  - Lower impurity level
  - Higher film density

PEALD limitations (compared to thermal ALD):

- More advanced and expensive ALD tool
- Deposition on one wafer at a time
- Reduced step coverage - Reactive plasma species decompose quickly
- Longer purge time
  - Larger chamber because of the plasma cone
- Plasma-induced surface damage (usually only a problem for direct plasma PEALDs)

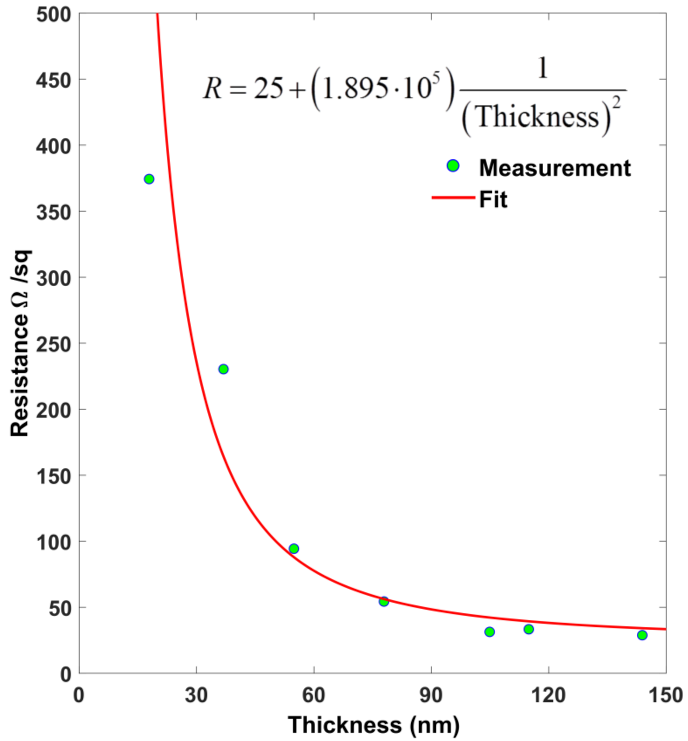
PEALD - Nitride depositions

Good quality nitride layers contain a very low amount of oxygen – and thus have low sheet resistance

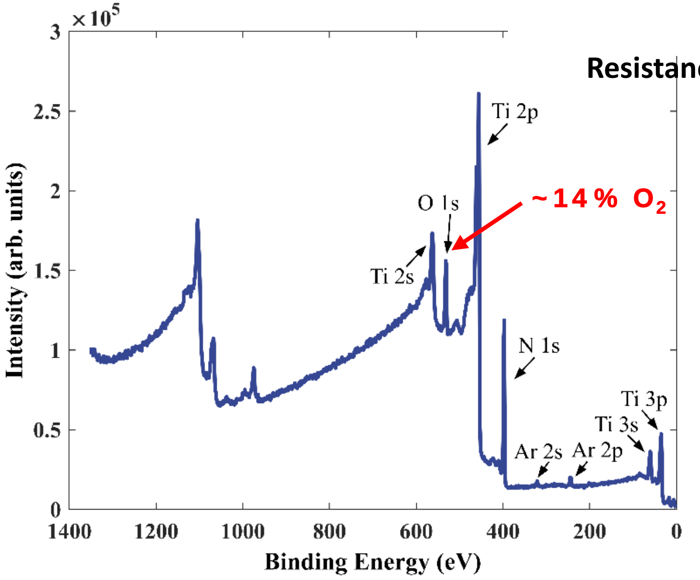
The sheet resistance denpends on thickness

PEALD nitride depositions at DTU Nanolab:

- Both oxides and nitrides are deposited in the same PEALD – but not at the same time. Still, nitride layers will contain small amounts of oxygen
- Switching from oxide to nitride depositions is very time consuming, because at least three days of passivation are needed



Resistance of TiN deposited on glass at 500 ˚C



XPS measurement of TiN deposited at 500˚C

ALD tools within the Nordic Nanolab Network

ALD tools within the Nordic Nanolab Network

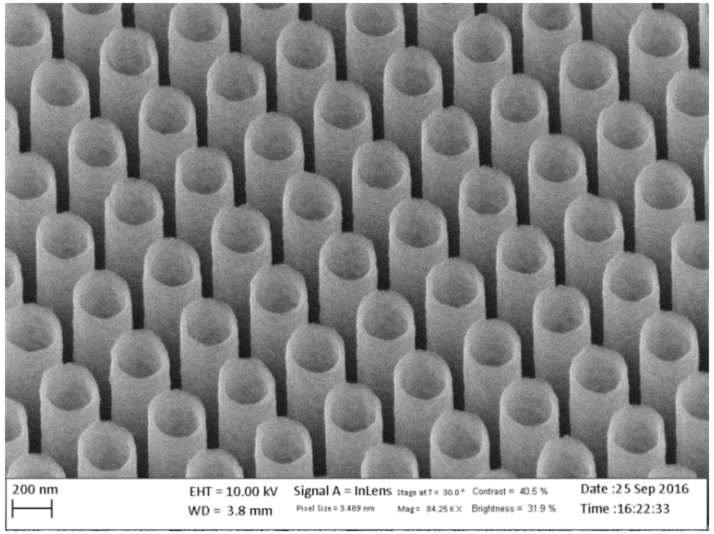
	Lab	ALD tool(s)
Lund, Sweden	Lund Nano Lab	Cambridge Fiji
		Cambridge Nanotech Savannah-100
		Picosun Sunale R-100
Göteborg, Sweden	Chalmers MC2	Oxford FlexAl
Uppsala, Sweden	Ångström	Microchemistry F120
		Picosun R-200
Stockholm, Sweden	KTH Electrum	Beneq TFS 200
Oslo, Norway	UiO MiNalab	Beneq TFS 200
Trondheim, Norway	NTNU Nanolab	Veeco Ultratech Savannah S-200
Helsinki, Finland	Allto / Micronova	2 * Beneq TFS500 ALD
		Picosun Sundale R-200
		ALD reactor SUNALE R-150B
Lyngby, Denmark	DTU Nanolab	Picosun R-200
		Picosun R-200 Advanced

ALD applications

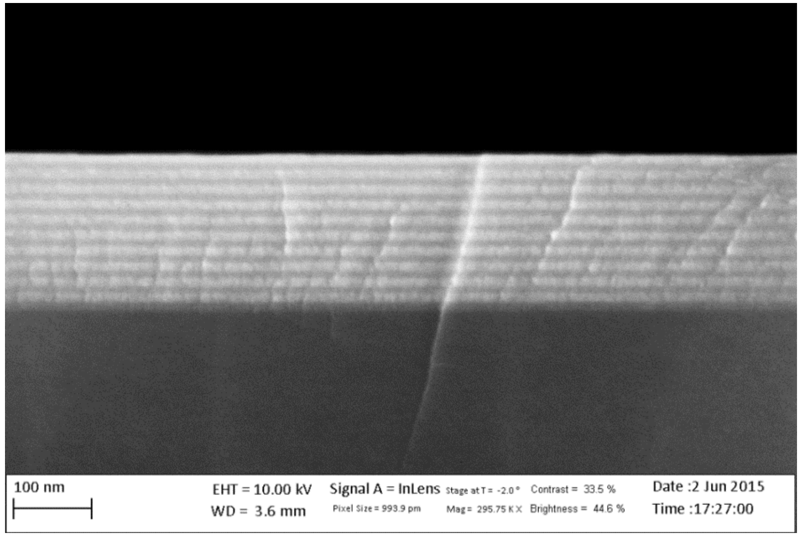
ALD - Applications

General application examples:

- Micromechanical systems (MEMS)
- 3D nanostructures
- Optical devices (e.g. waveguides and optical fibers)
- Isolating layers
- High-κ dielectric
- Back end of line (BEOL) processes
- Multilayer structures
- Piezoelectric layers (ZnO, AlN)
- Protection and encapsulation layers



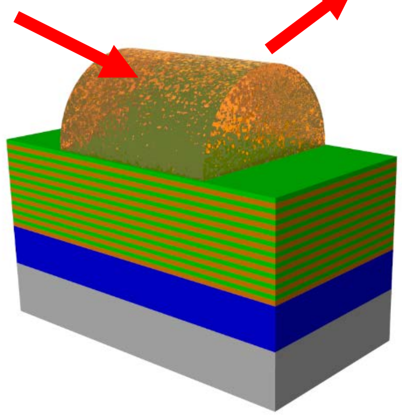
3D AZO (Al-doped ZnO) pillars made with ALD
AZO has been depositited on Si pillars that afterwards have been selectively etched away
Opt. Mater. Express 7(5), 1606-1627 (2017)

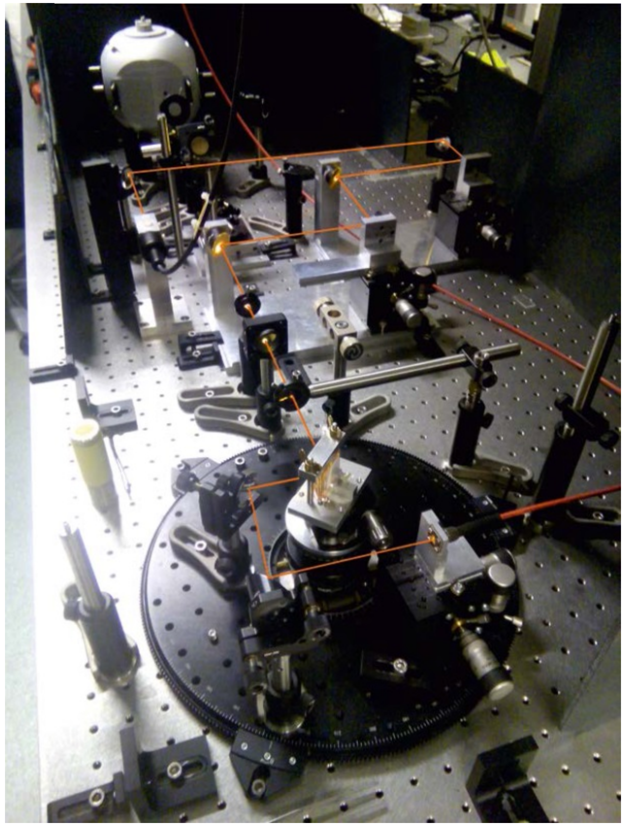


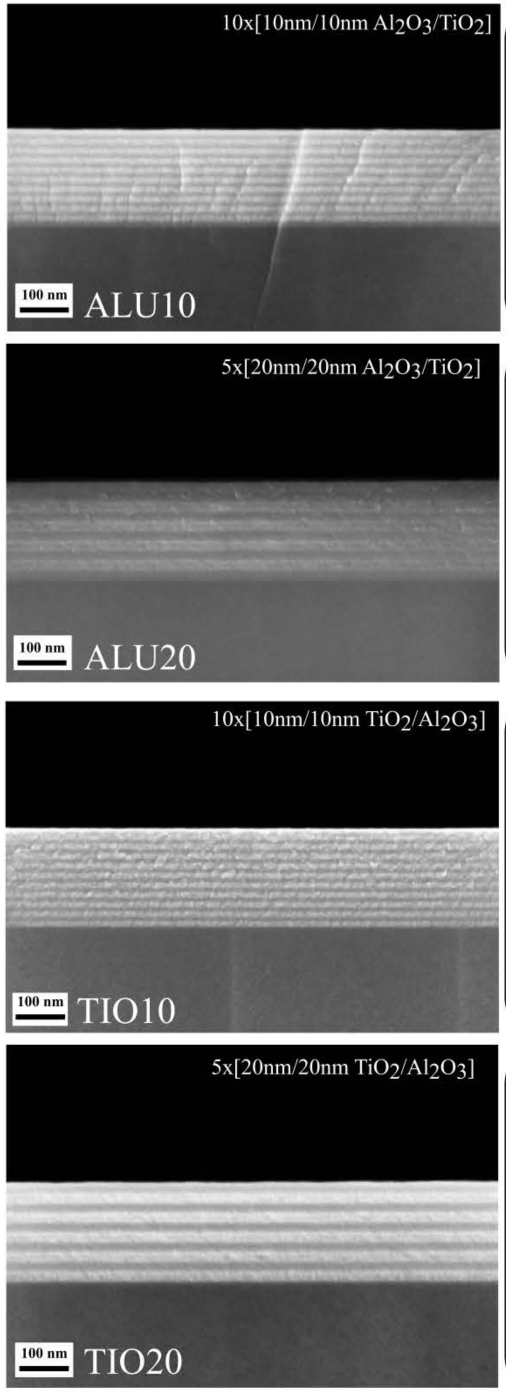
Si sample with multilayers of Al_2O_3 and TiO_2
Phys. Rev. Lett. 115, 177402 (2015)

Nordic Nanolab Network

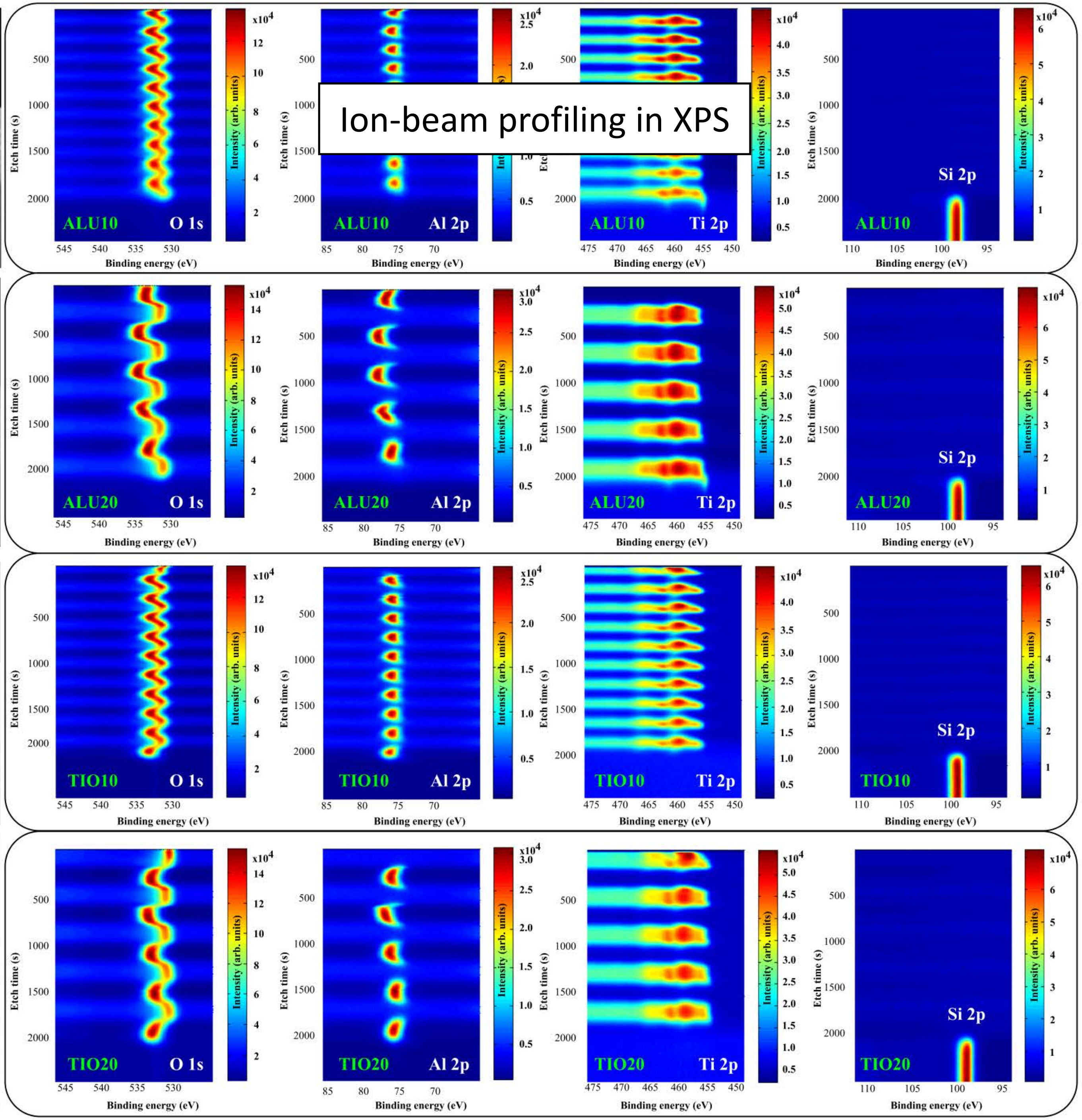
Phys. Rev. Lett. 115(17), 2015, 177402



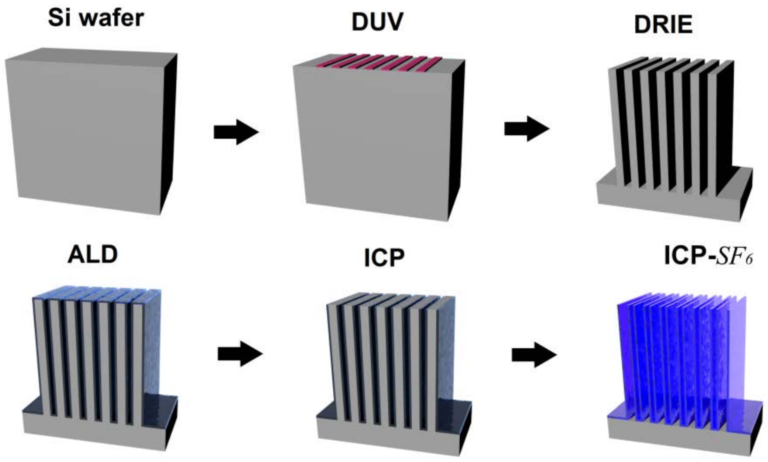




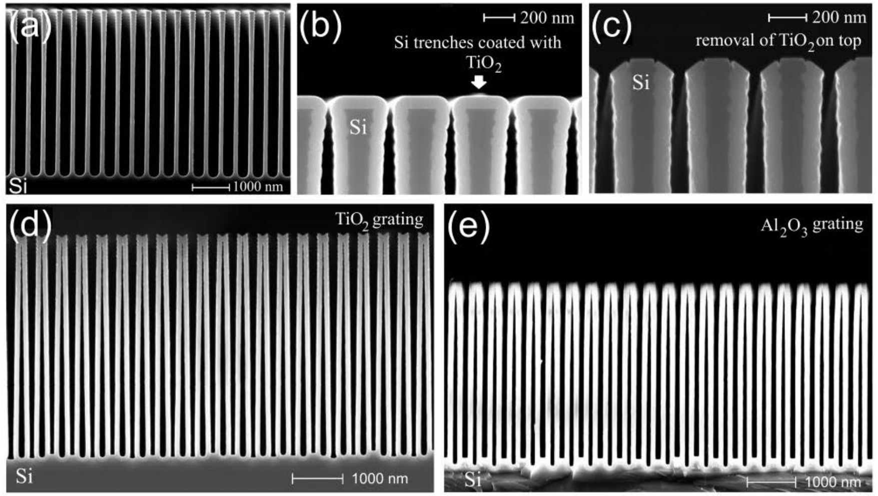
Ion-beam profiling in XPS



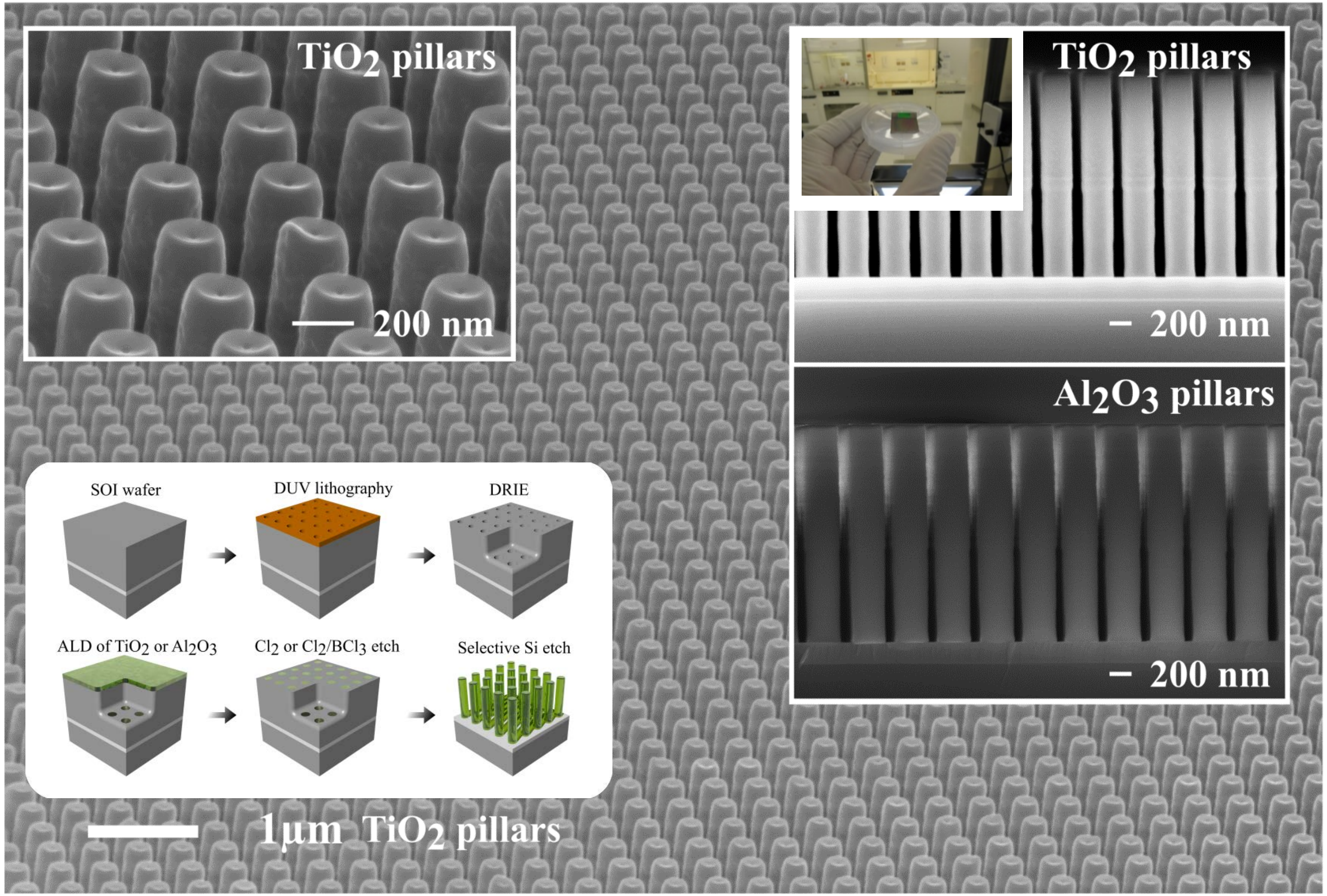
Vertically Arranged Al_2O_3 and TiO_2 Nanogratings and pillars



J. Vac. Sci. Technol. A 34(3), 2016 031605



(a) Fabricated silicon trenches. (b) TiO_2 ALD coating of trenches. (c) Selective opening of the top parts of the gratings. (d) Fabricated TiO_2 and (e) Al_2O_3 gratings.



Fabrication of TiO_2 and Al_2O_3 pillars. The concept and final realization.

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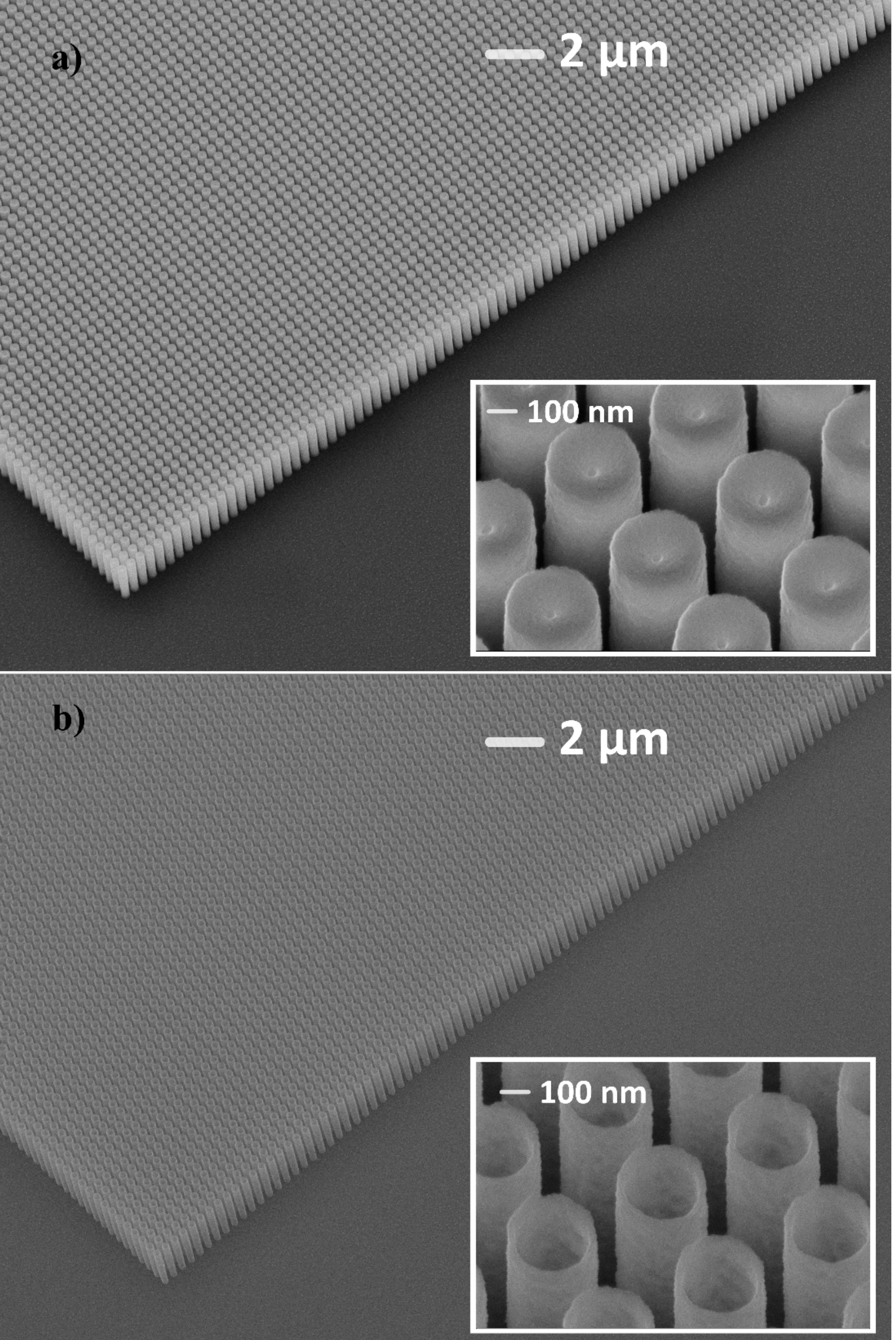
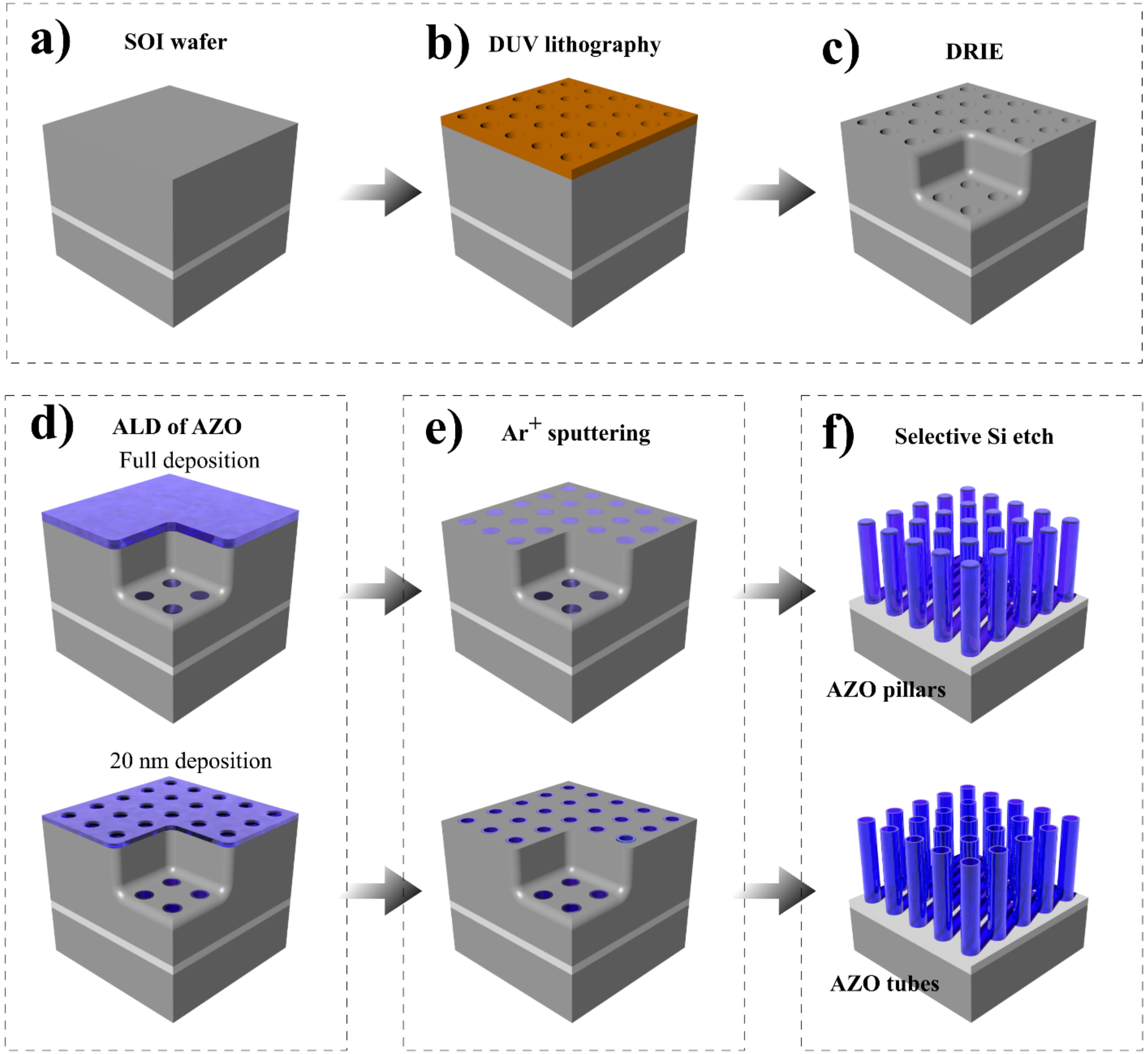


Al-doped ZnO nanopillars arrays as anisotropic metamaterials



Opt. Mater. Express 7(5), 2017 1606-1627

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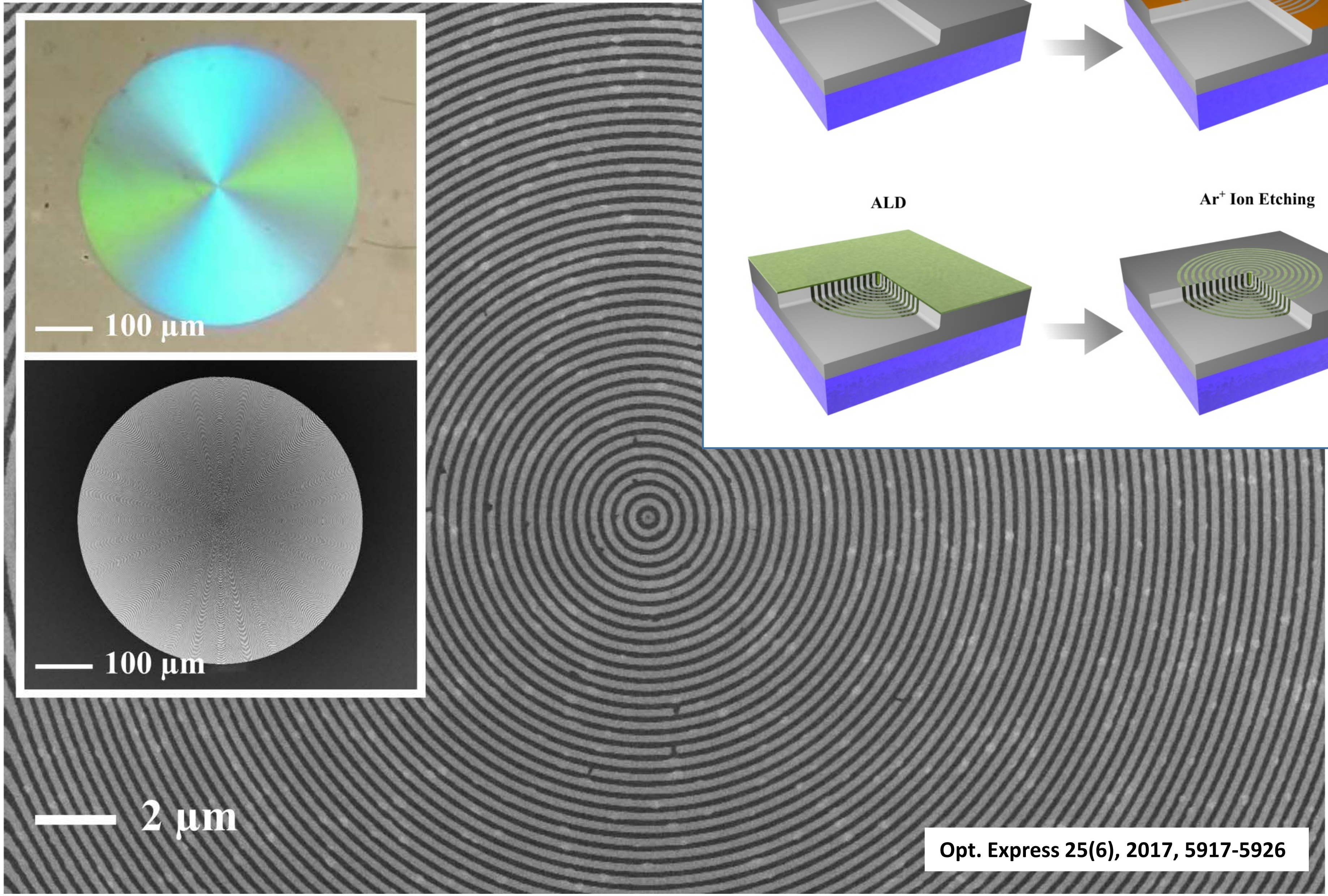
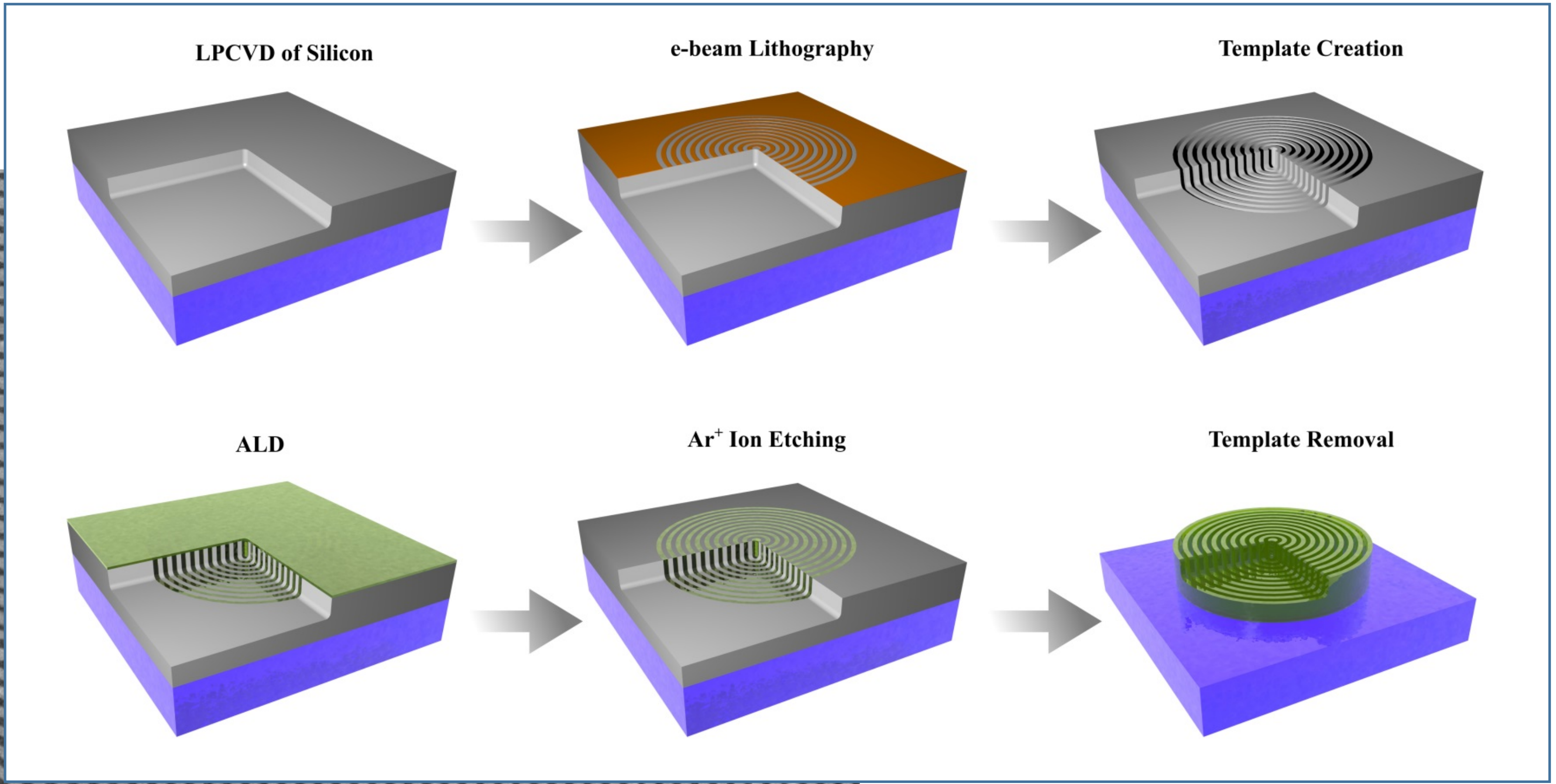
TiO_2 Concentric Rings (Q-plates)



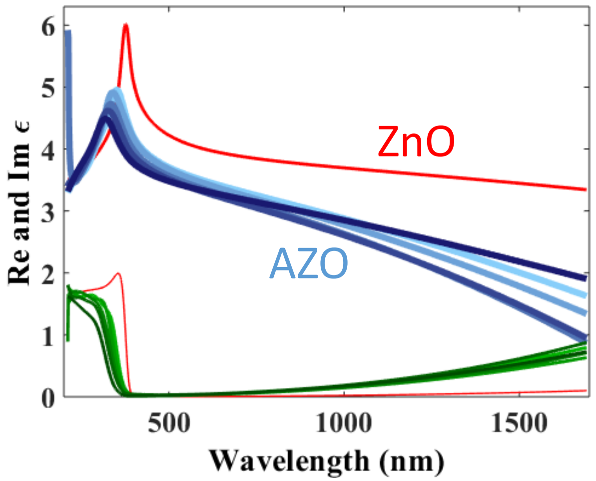


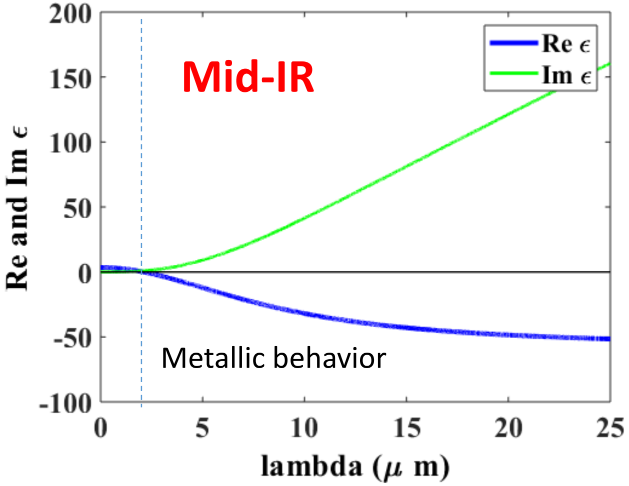
Opt. Express 25(6), 2017, 5917-5926

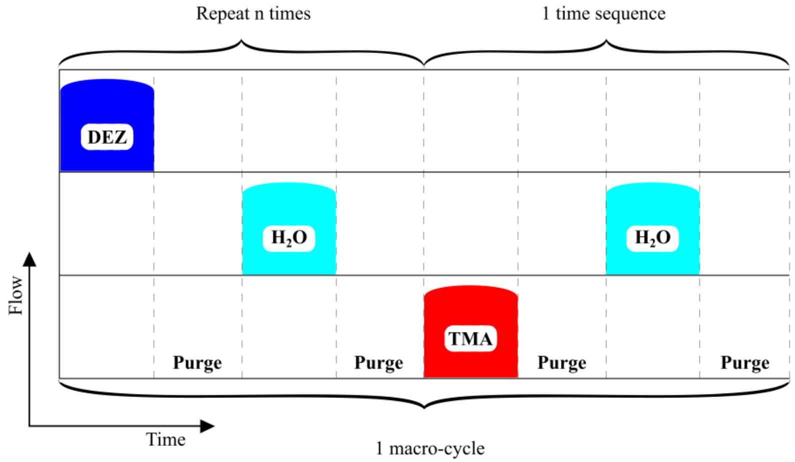
Plasmonic materials by ALD

When real permittivity ε(λ) becomes negative the material starts to behave as a metal.

Doping of ZnO (DEZ+H_2O) by Al. (AZO)



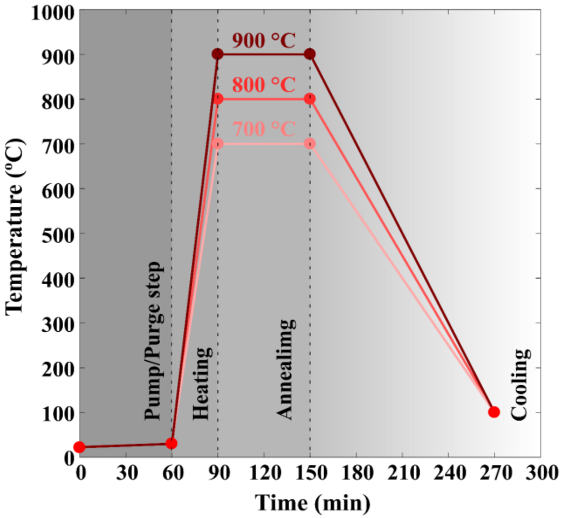


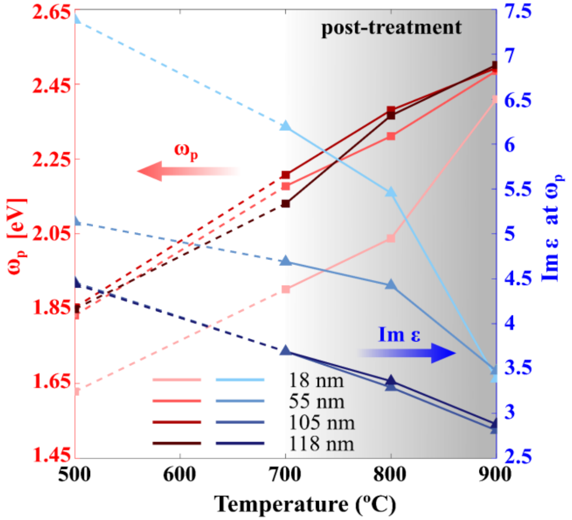


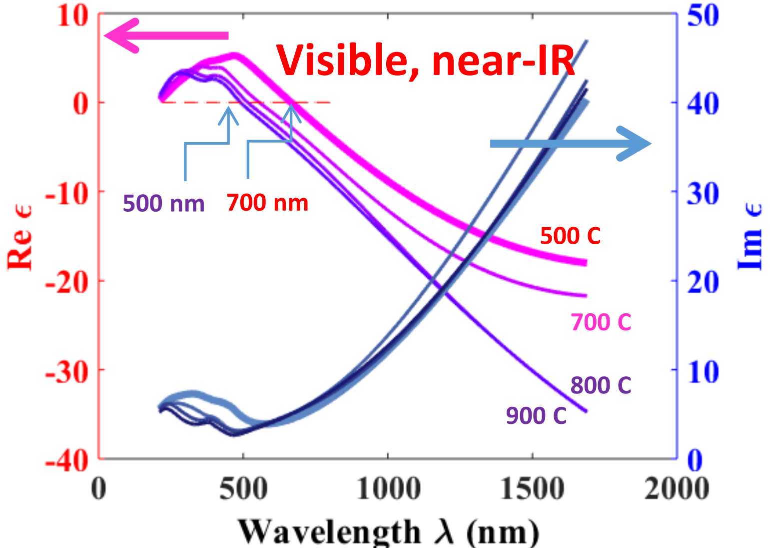
DEZ – diethyl zinc

TMA – trimethylaluminium

Post-treatment (annealing). Case of TiN ($TiCl_4$ +NH_3)





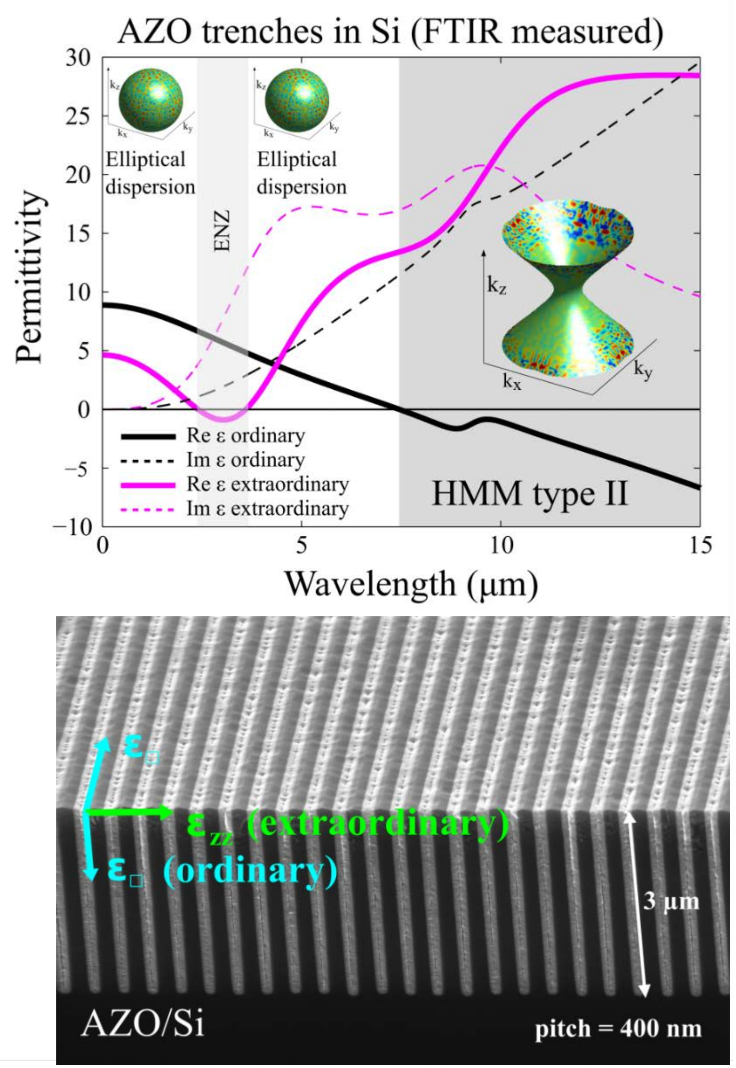


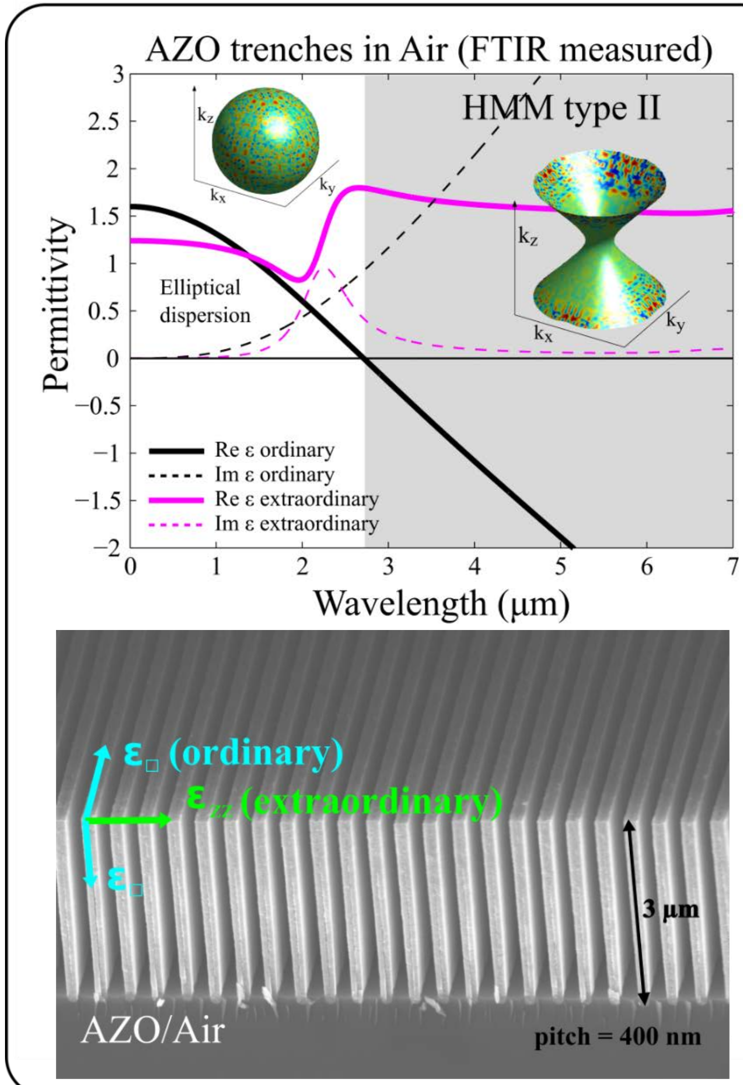
AZO trenches in Si and Air as hyperbolic metamaterial (HMM)

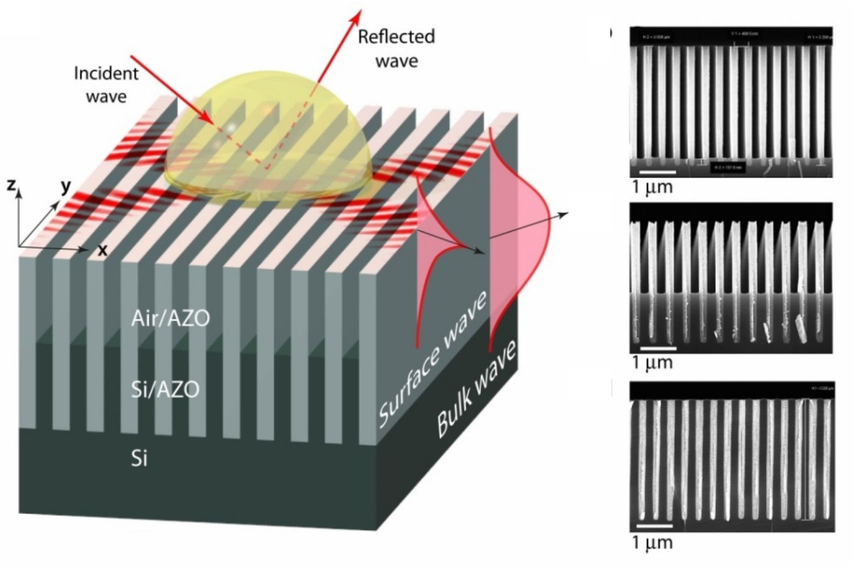
Effective Medium Theory (EMT):

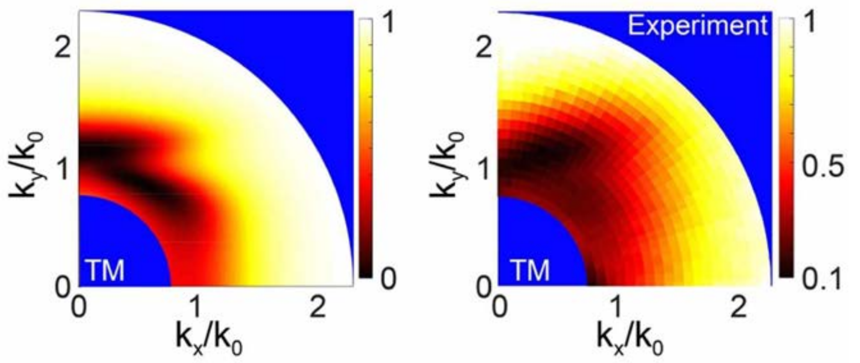
$$\varepsilon_{\square} = p_m\varepsilon_m + p_d\varepsilon_d \quad \varepsilon_{zz} = \frac{\varepsilon_m\varepsilon_d}{p_d\varepsilon_m + p_m\varepsilon_d}$$

ACS Photonics 4 (11), 2017 2899–2907

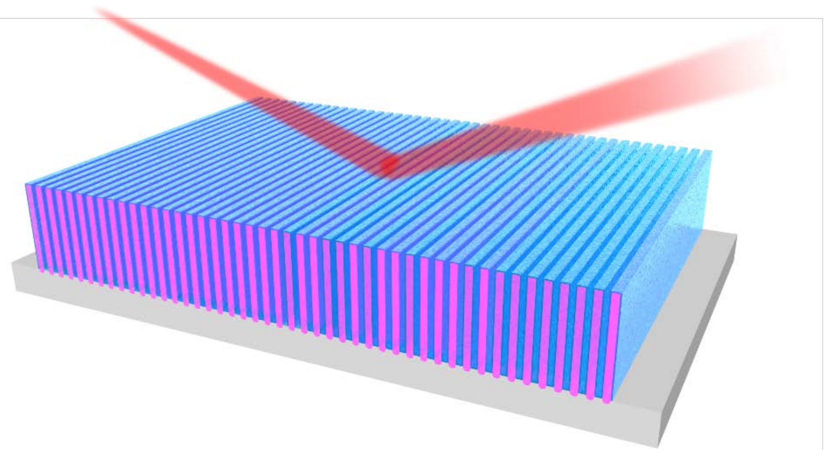




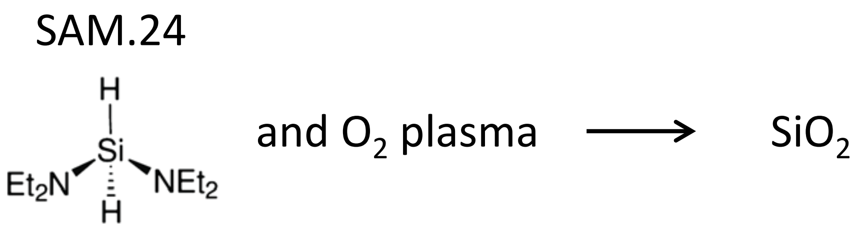


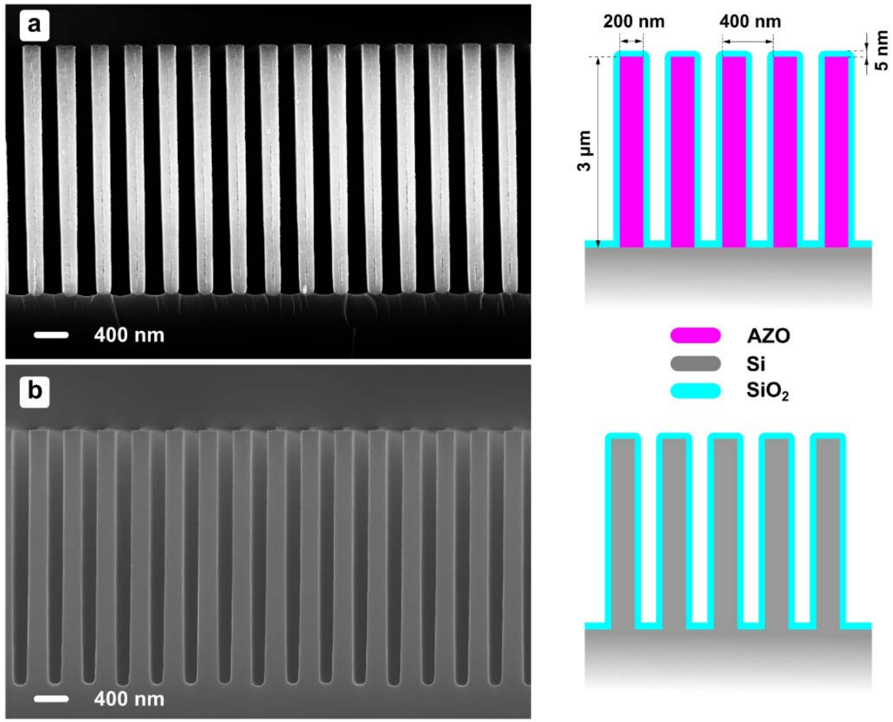


Hyperbolic metamaterials for mid-infrared sensing

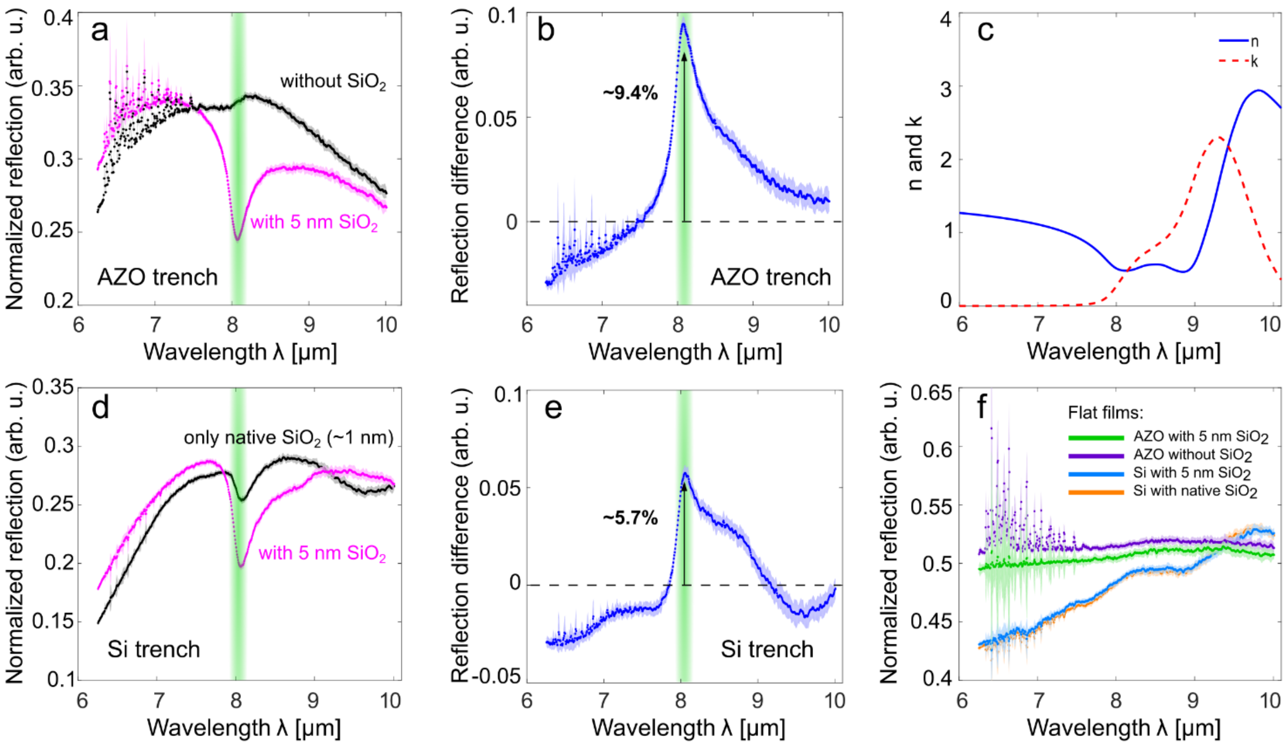


ACS Appl. Nano Mater. 1(3), 2018, 1212–1218





Cross-sectional SEM images of (a) fabricated AZO-based HMM structures and (b) Si trenches, as well as corresponding schematic illustrations of AZO and Si trenches with 5 nm thick SiO2 (not visible in SEM images), respectively.



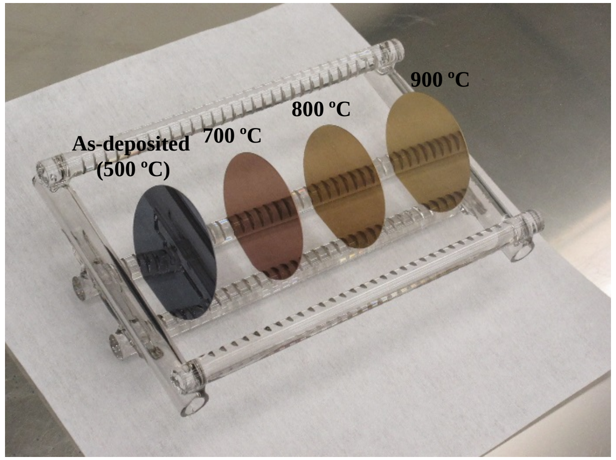
Observation of absorption enhancement. (a) Measured free-space reflection of AZO trench structures with (dotted pink) and without (dotted black) the 5 nm thick SiO2 layer. (b) Reflection difference. (c) Real (n) and imaginary part (k) of the refractive index of SiO2. (d) Measured reflection of Si trench structures with (dotted pink) and without (dotted black) the 5 nm thick SiO2 layer. (e) Reflection difference. (f) Reflection from flat surfaces.

TiN grating as plasmonic biosensor

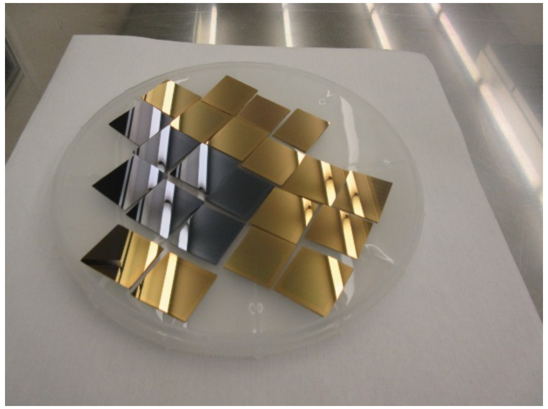
Opt. Mater. Express 7(11), 2017 4171-4182

Sensing the refraction index contrast.

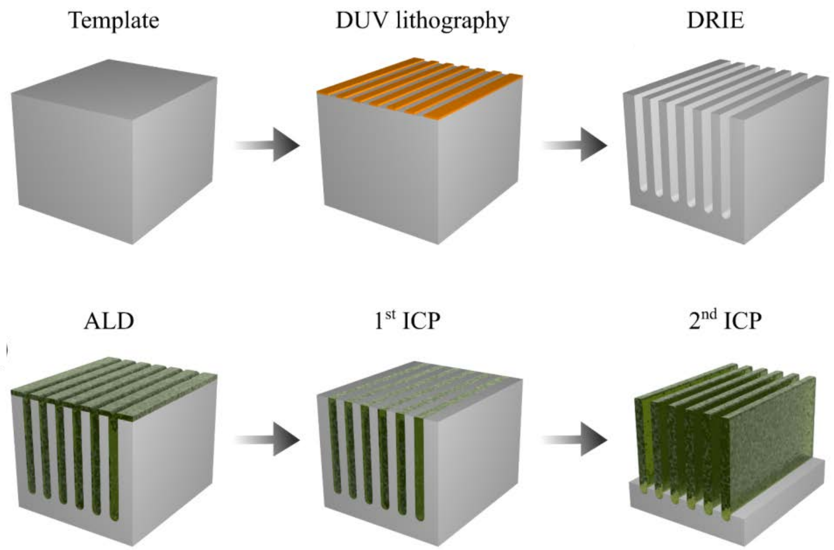
TiN becomes plasmonic at λ=500nm (visible light)

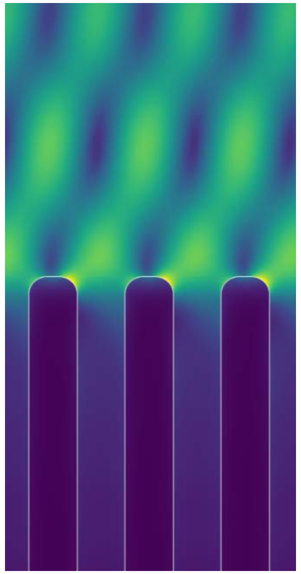


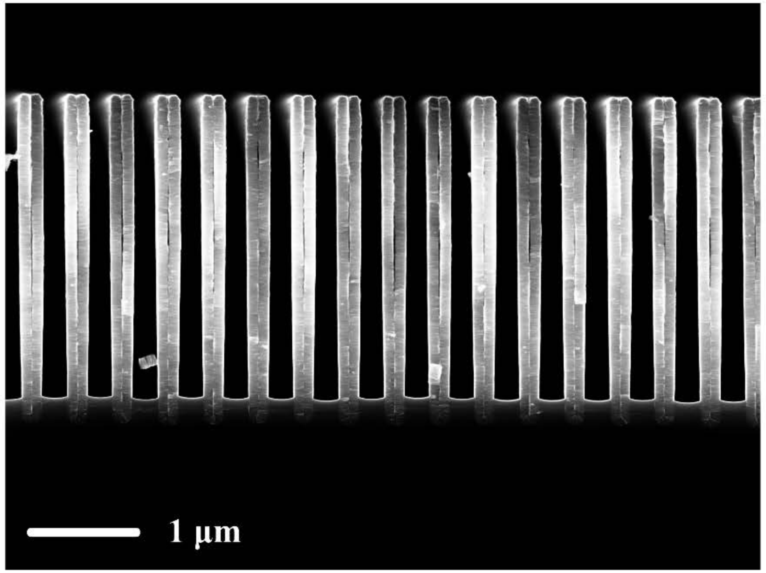
TiN as deposited at 500 ºC and as result of post treatment.
Annealing at different temperatures from 700 ºC to 900 ºC.

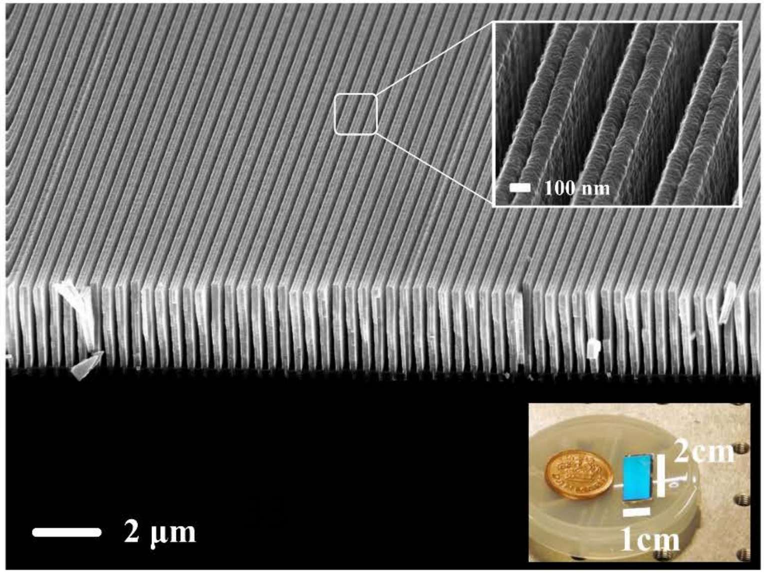


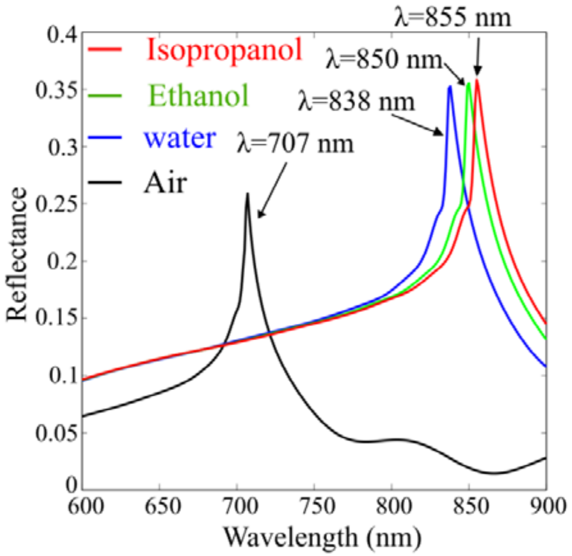
Si trench template covered with TiN before and after annealing at 900 ºC.
Silver and gold colored chips, respectively.











Thanks for your attention

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