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Materials Science and Technology

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Haute Ecole Spécialisée de Suisse occidentale
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University of Applied Sciences and Arts Western Switzerland

Master of Science HES-SO in Life Sciences

Plasma Enhanced ALD of Titanium Nitride on Complex Shapes

Franck Genilloud

CHEMICAL DEVELOPMENT & PRODUCTION

HEIA-FR

Advisors: Dr. Pierre Brodard & Dr. Ivo Utke // In collaboration with **EMPA, Thun**

Introduction and Objectives

Atomic Layer Deposition (ALD) is a pivotal technique for creating thin films with unparalleled precision, offering atomistic control over film thickness and conformality. Essential for manufacturing advanced semiconductors in today's electronic devices, ALD's capabilities are unmatched. This thesis delves into Plasma-Enhanced Atomic Layer Deposition (PEALD), an advancement that integrates a plasma source to improve the ALD process. This innovation expands the material deposition spectrum, reduces temperatures required for deposition and enhances film quality, but also introduces new process development challenges. This thesis aimed to understand and optimise the PEALD deposition of titanium nitride to achieve high quality film depositions on 3D structures.

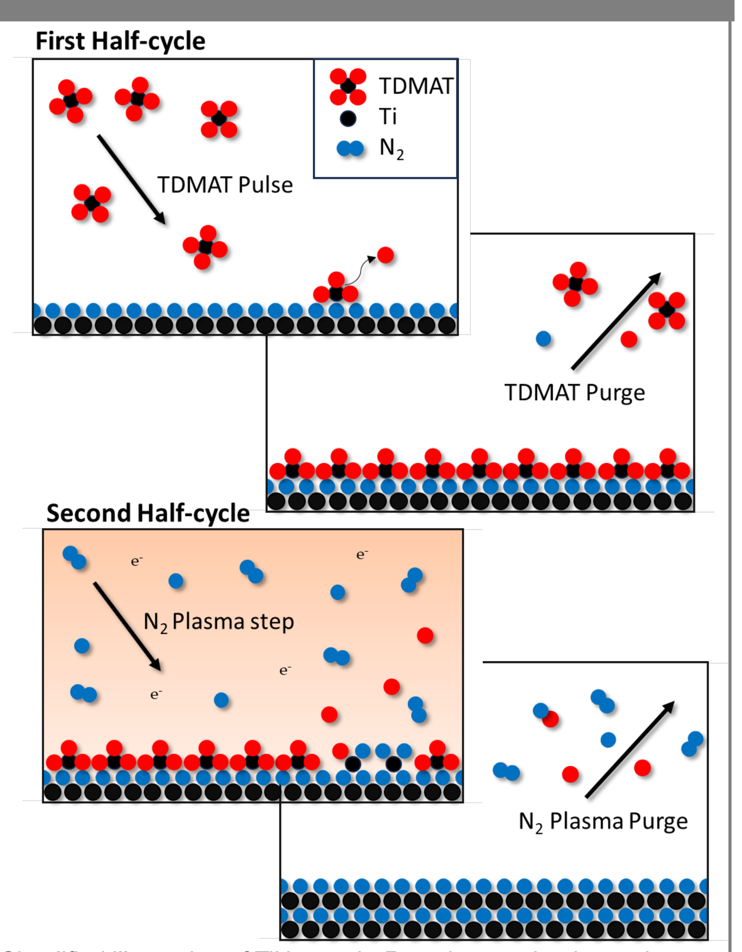
Materials and Methods

ALD's strength lies in sequential self-limiting surface reactions that ensure only one atomic layer is deposited in each cycle. For this process to function, precise control of temperature, pressure and timing is essential.

Swiss Cluster

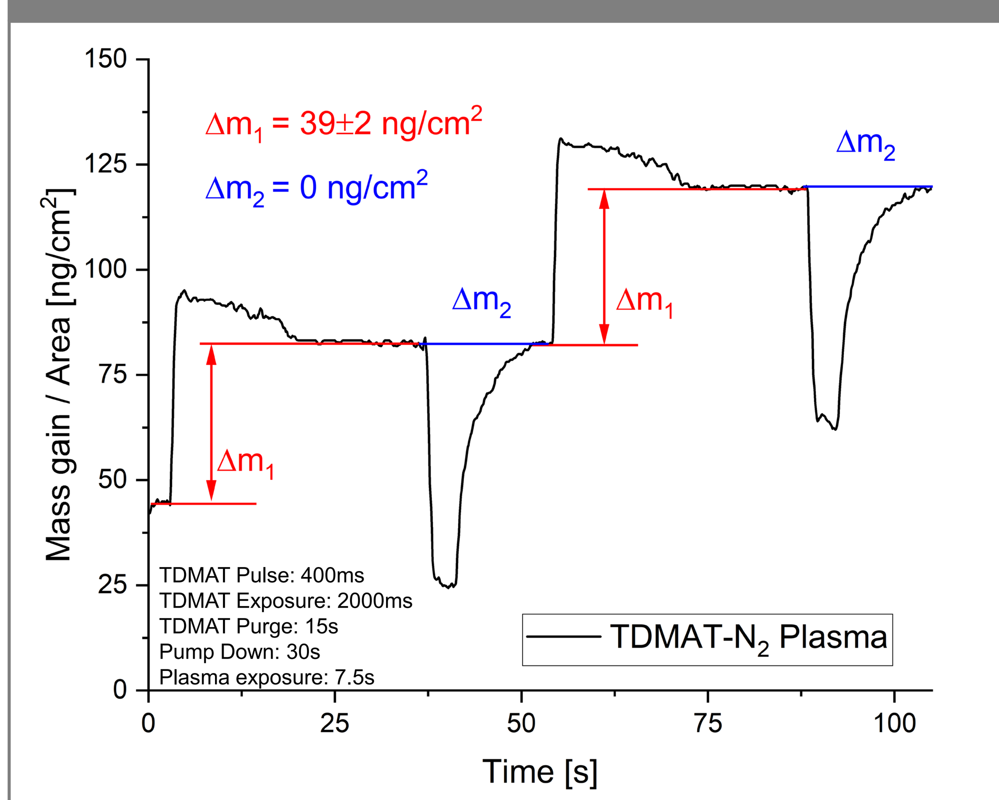
Image from Swiss Cluster AG

To control all these variables, an ALD reactor from Swiss Cluster was used. The vacuum chamber is equipped with precise thermal control, microwave plasma sources and the modular panels were swapped for either a Time-of-Flight Mass Spectrometer (TOFMS) adapter or a Quartz Crystal Microbalance (QCM).



Simplified illustration of TiN growth. Reaction mechanism unknown.

In-Situ QCM analysis of TDMAT-N_2 plasma

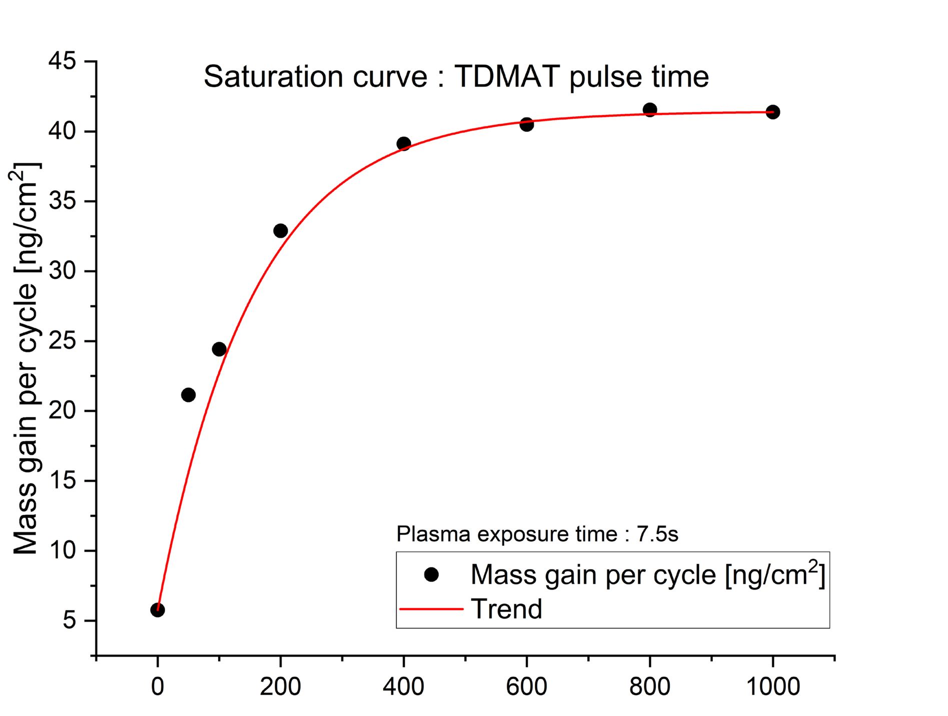


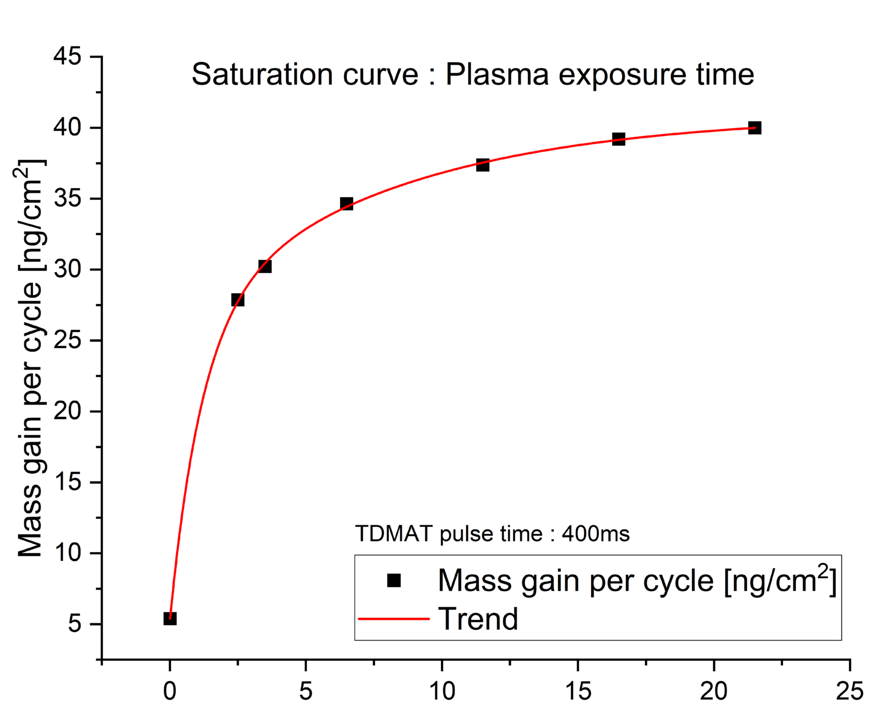
Step	Calculated mass gain [ng/cm²]	Measured mass gain[ng/cm²]
$Ti(DMA)_3$ ↓ Δm1	38.1	39
DMA ↑ NH_2↓ Δm2	-11.8	0
ALD Cycle total	141[a]	39

a: Expected GPC of crystalline TiN [3]

By calculating the expected growths per half-cycle, the process can be compared to the assumed reactions. Here, the significant difference in mass gain per TiN cycle is due to steric hindrance with the TDMAT molecule.

Using a QCM is the fastest way to determine ideal parameters for saturation.
Optimised timings for this process: 400ms TDMAT pulse and 7.5 seconds of plasma exposure.

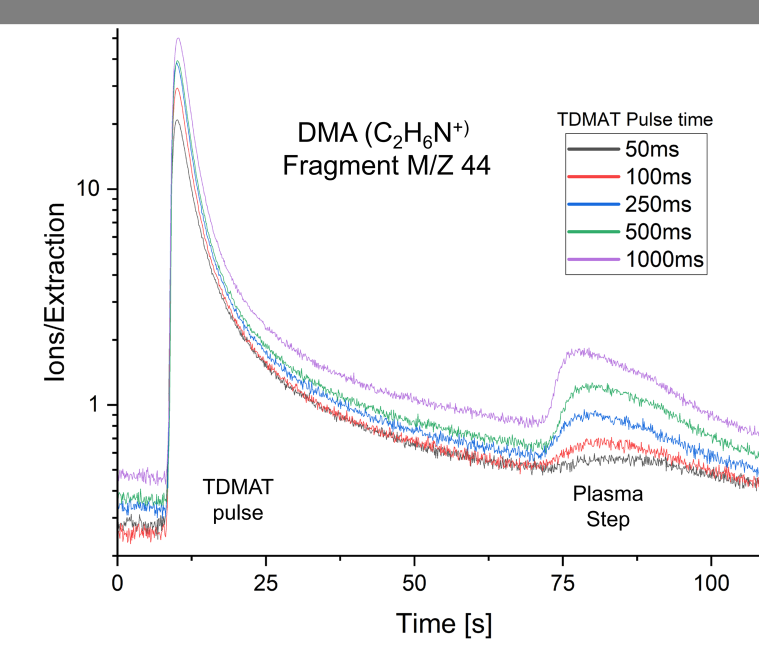


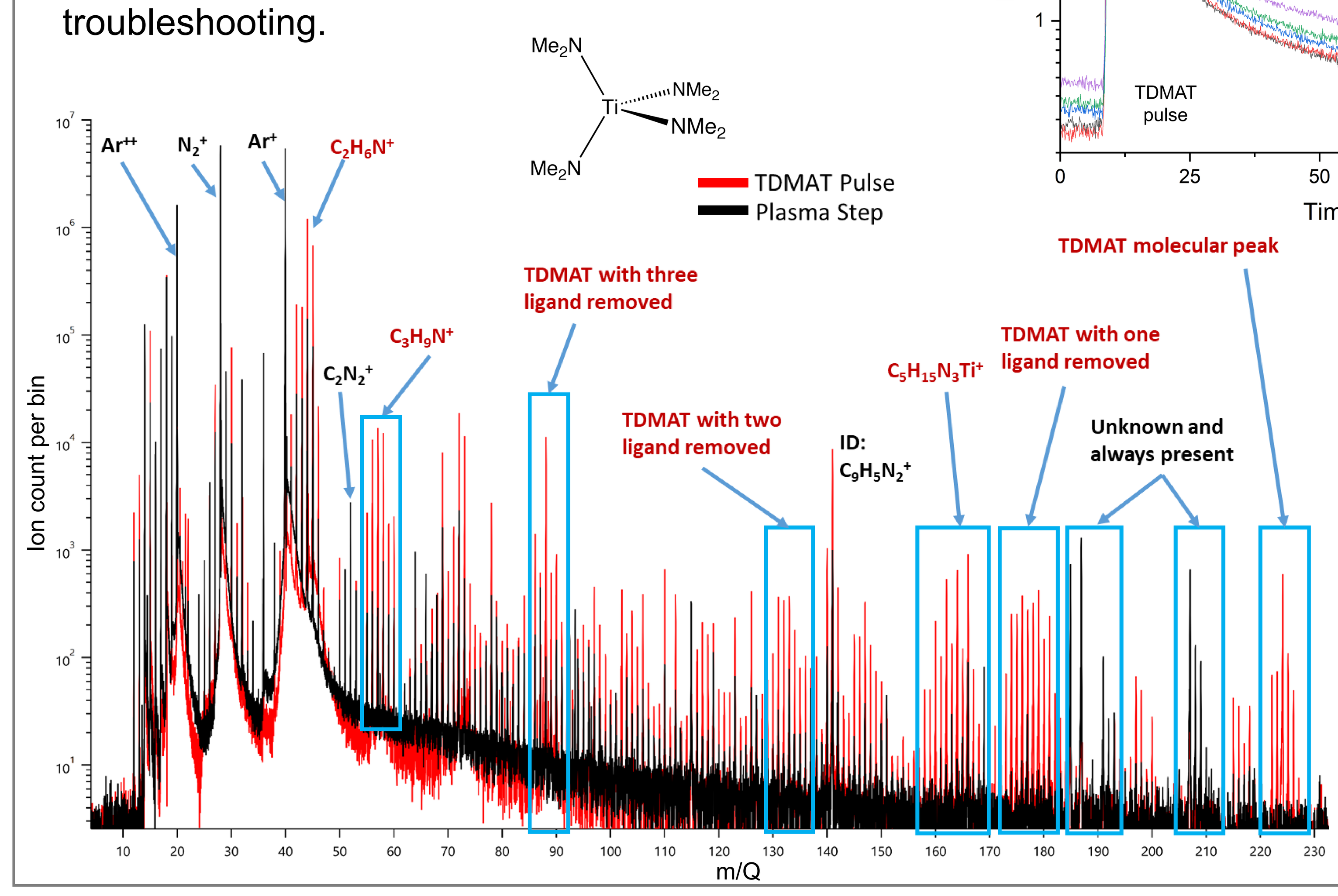


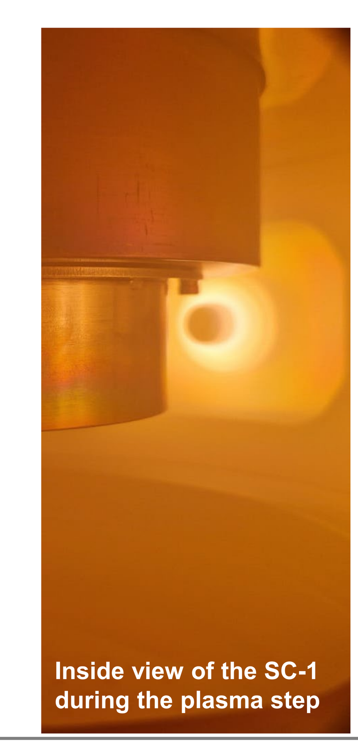
TOFMS investigation of TiN deposition

TOFMS Opens a window into the surface reaction products and species generated during the TDMAT pulse and the plasma step.

It is not only used to understand the chemistry, but also invaluable in process development and troubleshooting.







Film depositions on Complex shapes

Films on flat wafers

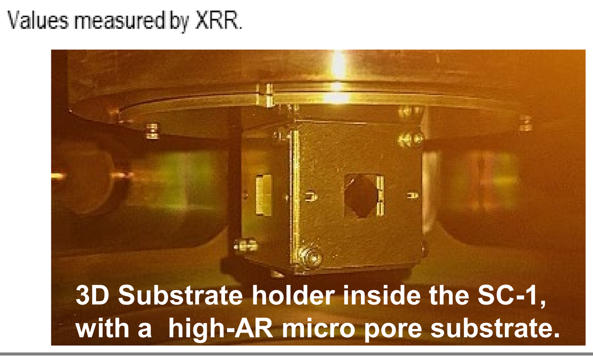
Recipe	Density [g/cm³]	GPC [Å/cycle]	Uniformity [%][a]
Prev. recipe	3.03	1.35	80.9
New recipe	4.7	0.61	96.8
literature	4.23-5[b]	0.5-1[b]	-

a : Coefficient of Variation method on thickness, measured on 5 points by XRR.
b : Bulk density of TiN : 5.4 g/cm³ [1], [2]

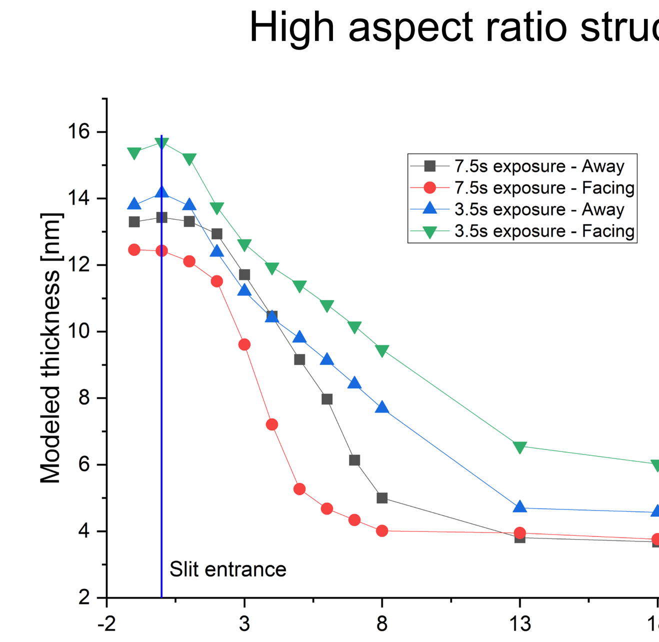
Films on cube substrate

Substrate face	Density [g/cm³]	GPC [Å/cycle]
Top	4.55	0.58
Inlet	4.61	0.60
QCM	4.85	0.61
Window	5.01	0.57
Outlet	4.87	0.56

Values measured by XRR.

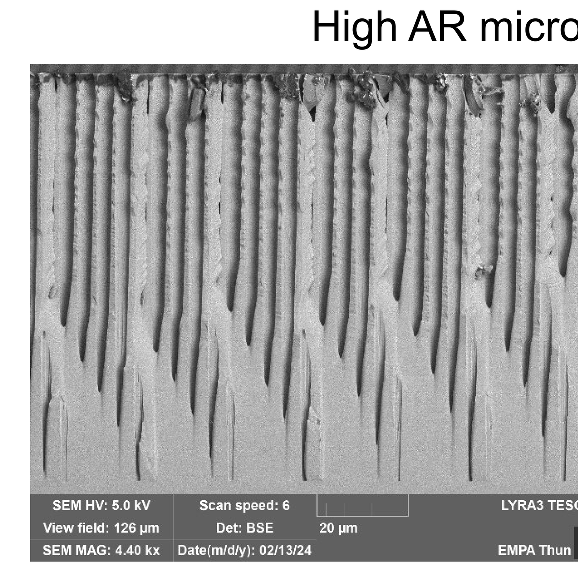


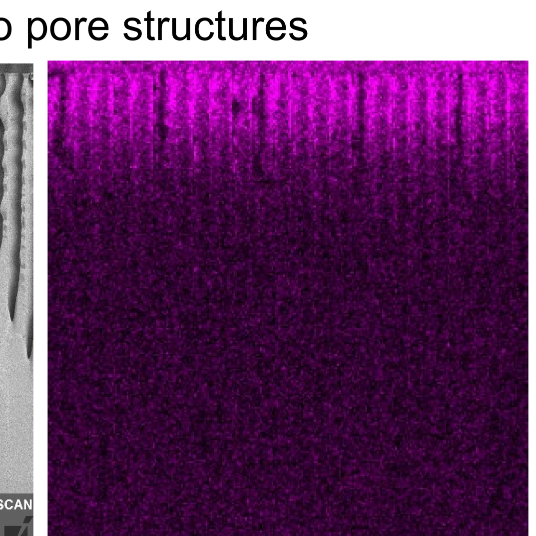
High aspect ratio structures (AR100)



Stacked high-AR structure

High AR micro pore structures





Purple : Ti signal (EDX)

Conclusion

By studying film deposition with *in-situ* instruments, the growth of TiN by PEALD is now better understood and the ideal process parameters for 2D depositions were found by saturation curves experiments. The effect of the direct plasma exposure was discovered to cause uneven deposition and lower conformality in some cases. Moreover, shielding the substrate was found to drastically enhance film uniformity on flat wafers. Overall, the deposition of high-density crystalline titanium nitride proved successful on 2D and simple 3D geometries. However, the film properties were found to significantly degrade inside high AR structures. Finally, additional research on high AR structures investigating deposition temperature and using longer exposure times could yield better results.

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[1] Shearrow, A. *et. al* Atomic Layer Deposition of Titanium Nitride for Quantum Circuits. *Appl Phys Lett* **2018**, *113* (21).
[2] Yemane, Y. *et al.* Superconducting Niobium Titanium Nitride Thin Films Deposited by Plasma-Enhanced Atomic Layer Deposition. Supercond Sci Technol **2017**, 30 (9).
[3] Thin Solid Films Volume 436, Issue 2, 31 July 2003, Pages 145-156

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