Atomic layer deposition for modification of surface properties

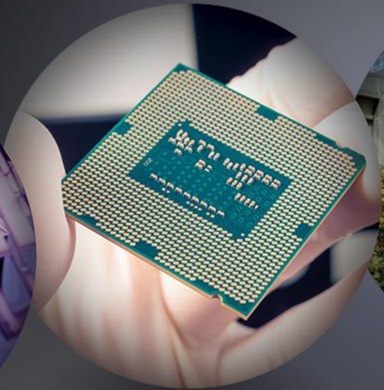
Dr. Emma Salmi and Kari Härkönen

Beneq


beneq
95
km/h
7213
RPM
Services
Equipment
Displays

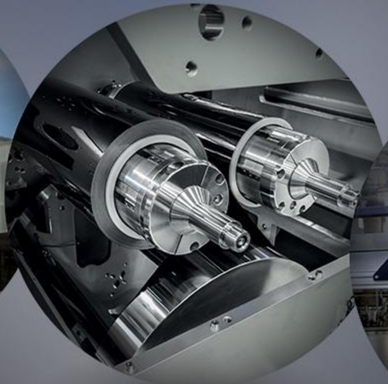
One Stop for All ALD

Research



Development Services

Coating Services



Industrial Equipment

Customer Services

Outline

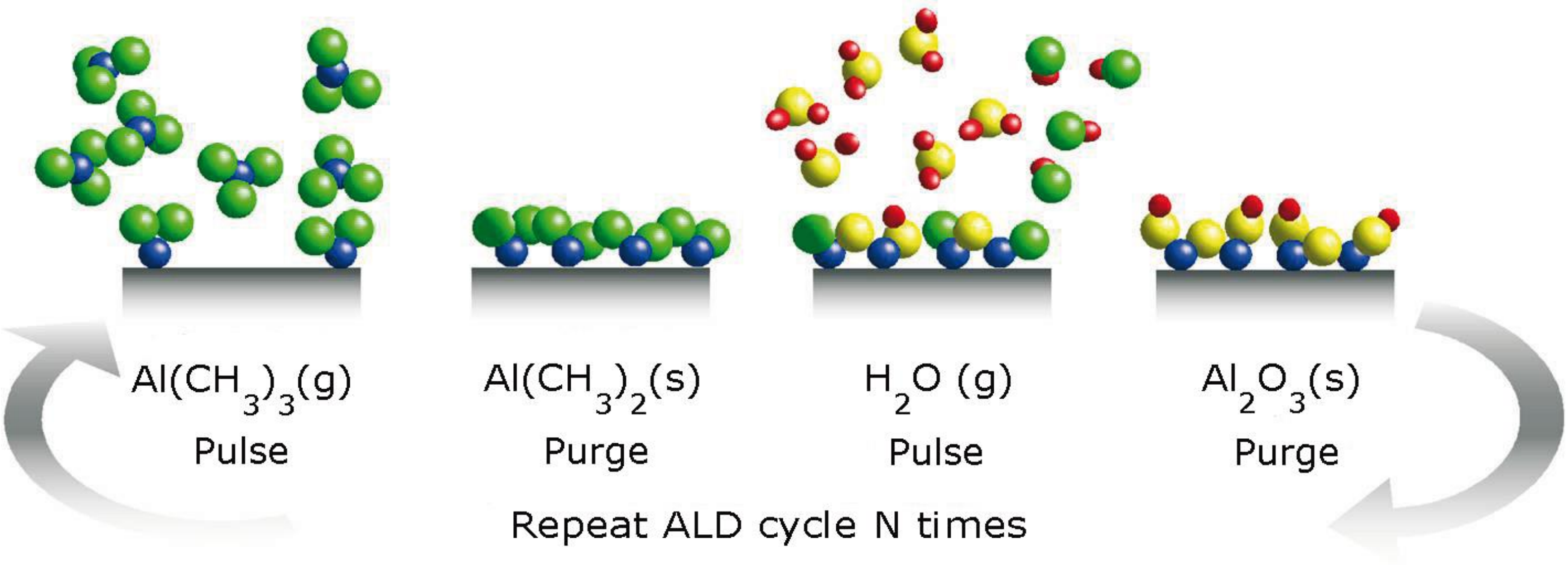
- Atomic layer deposition
- Surface modification with atomic layer deposition
  - Case I
    - TiN_x, $Ti(Al)C_x$ and $Ti(Al)N_xC_y$ on 304L SS
  - Case II
    - Al doped ZnO
- Conclusions

Atomic layer deposition

- Precision thin film deposition technique based on chemical vapor deposition
- First industrial application was electroluminescent displays
  - Manufactured in Finland since the 1980´s
  - Currently by Lumineq (Beneq)

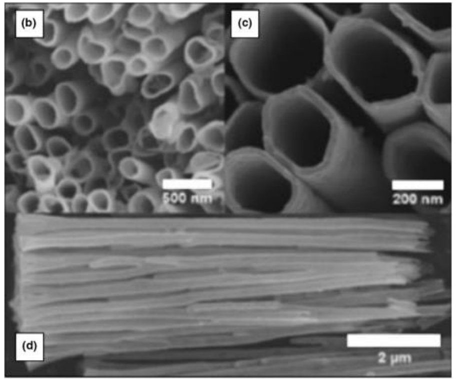


ALD – Mechanism

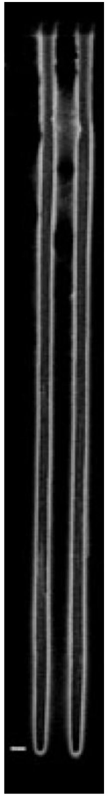


ALD – Advantages

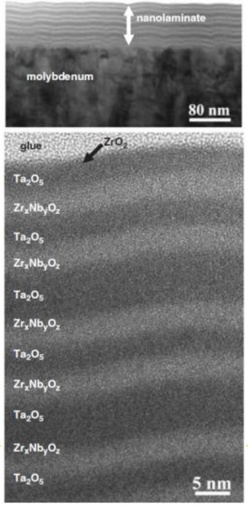
- Conformality and large area uniformity
- Control over thickness and composition
- Low defect density
- Reproducability
- Low thermal budget



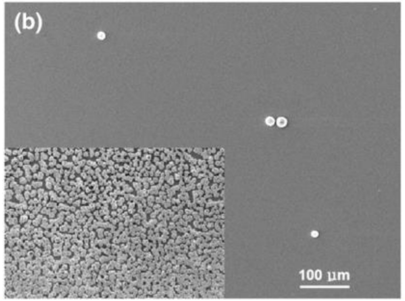
V. Pore et al., J. Am. Chem. Soc. **131** (2009) 3478



R.G. Gordon et al., Chem. Vap. Deposition, **9** (2003) 73



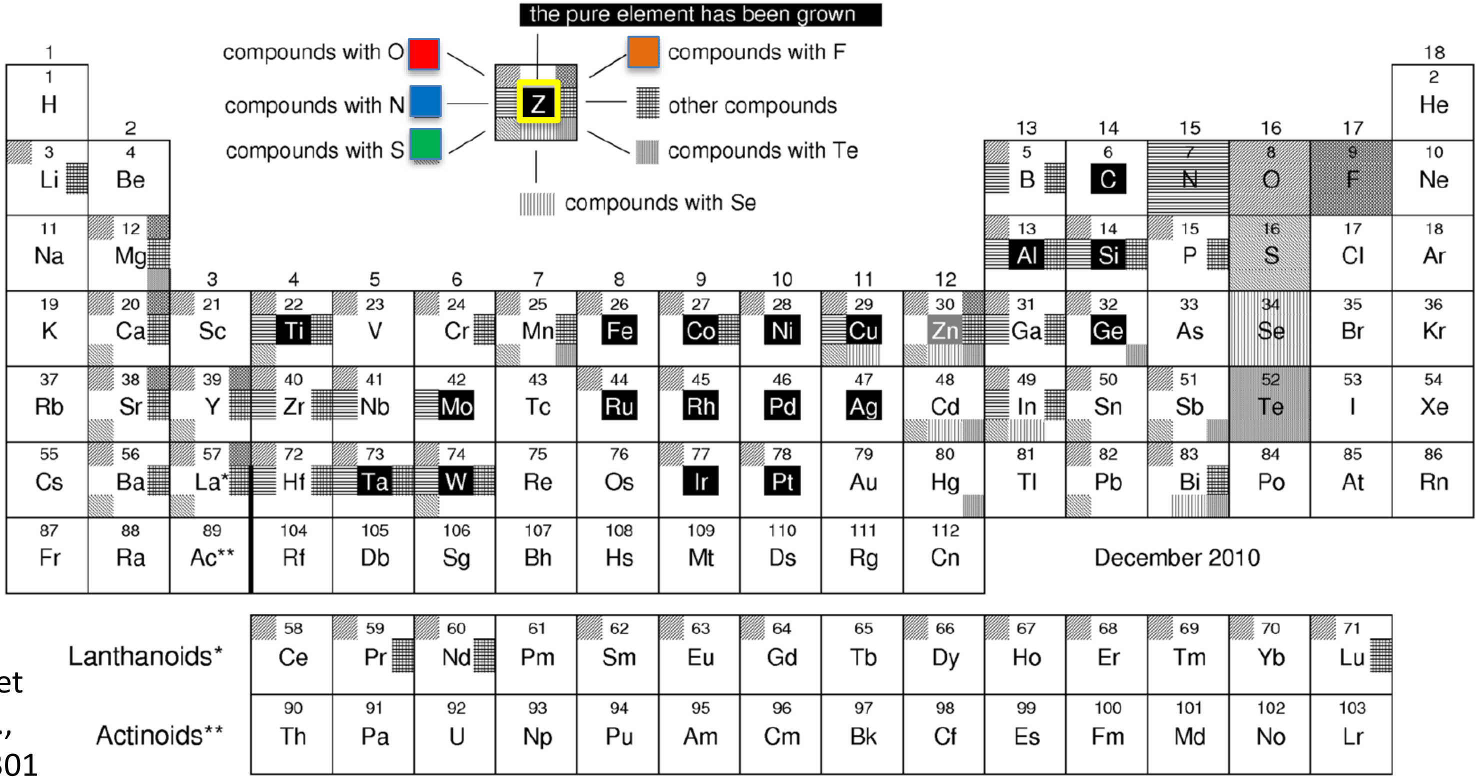
M. Leskelä et al., Mater. Sci. Eng. C, **27** (2007) 1504



Y. Zhang et al., Surf. Coat. Technol., **205** (2011) 3334

ALD – Available materials

2013

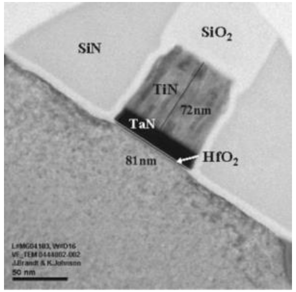


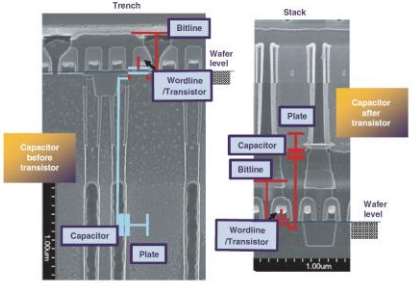
V. Miikkulainen et al., J. Appl. Phys., 113 (2013) 021301

ALD – Applications

Electroluminescent displays

Integrated circuits





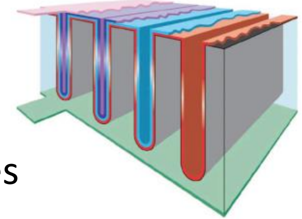
Permeation barriers

Protective coatings

Photovoltaics

Optical coatings

Batteries



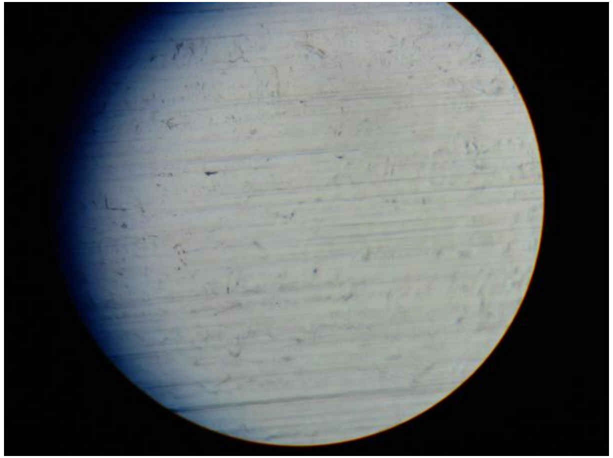
Case I

- TiN_x, $Ti(Al)C_x$ and $Ti(Al)N_xC_y$ thin films
  - Substrate 304L stainless steel
  - ALD film growth
    - Precusors
      - TiN_x from titanium tetrachloride ($TiCl_4$) and ammonia (NH_3)
      - $Ti(Al)C_x$ from titanium tetrachloride ($TiCl_4$) and trimethyl aluminium (TMA)
      - $Ti(Al)N_xC_y$ from $TiCl_4$, TMA and NH_3
    - Deposition temperature 430 °C
  - Coating thickness 100 nm

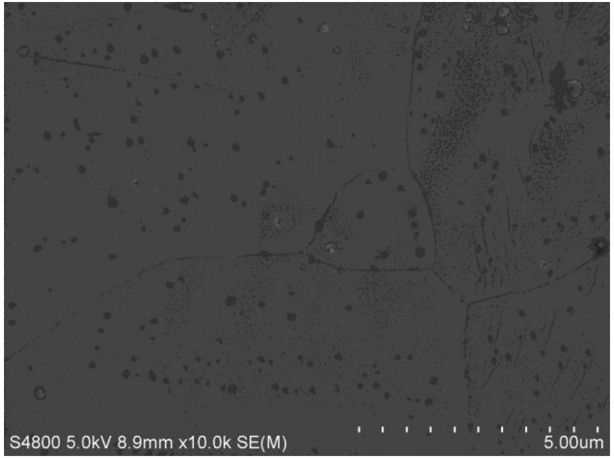
TiN$_x$, Ti(Al)C$_x$ and Ti(Al)N$_x$C$_y$ – Microscopy

- Uncoated 304L stainless steel
  - Rough surface morphology

1:2.5



1:50

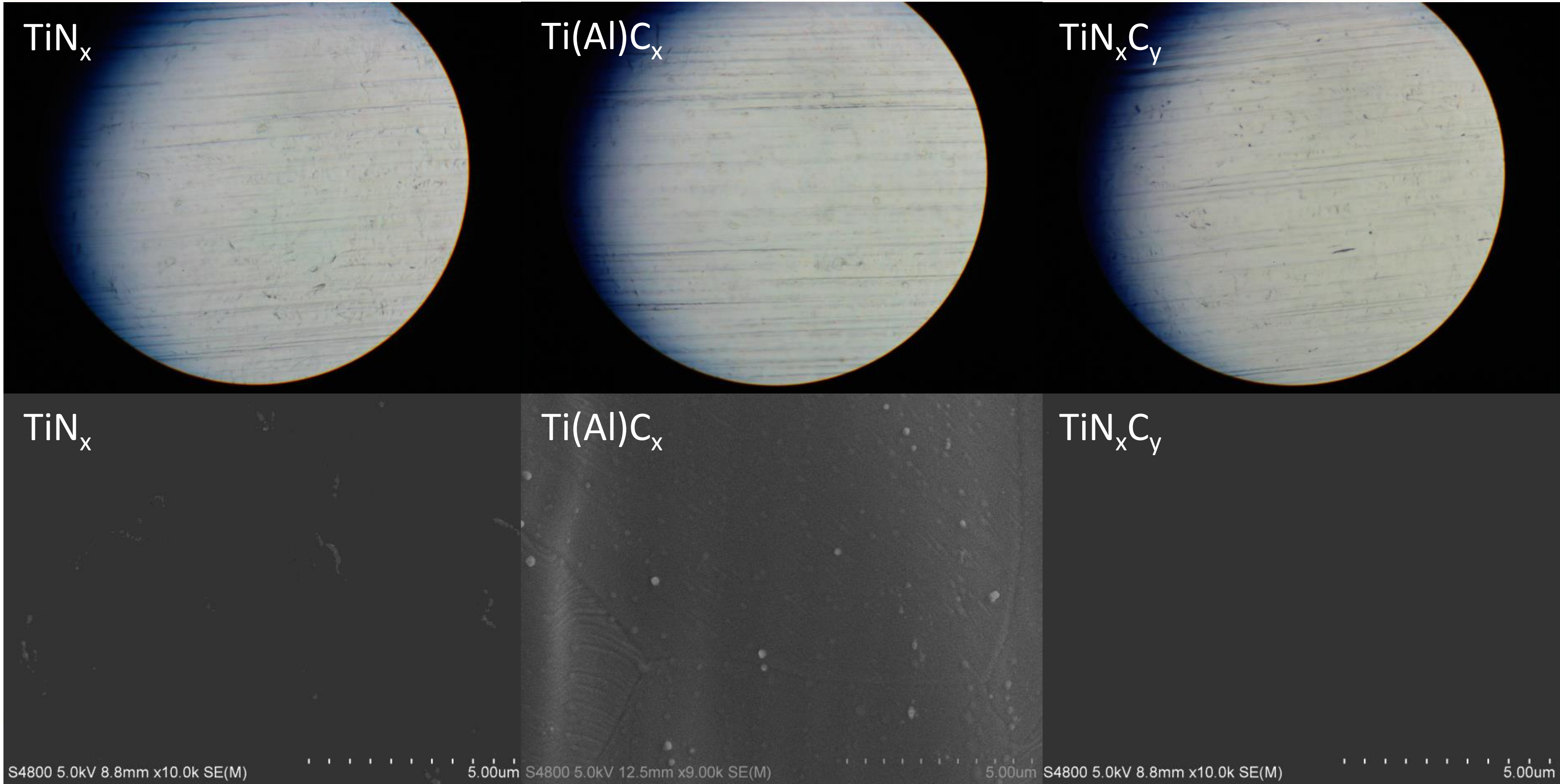


SEM

TiN_x, $Ti(Al)C_x$ and $Ti(Al)N_xC_y$ – Microscopy

Optical microscope

SEM



TiN_x, $Ti(Al)C_x$ and $Ti(Al)N_xC_y$ – Hydrophobicity

- The O_2 plasma treatment was used to oxidise the film surface

➡ Hydrophilicity

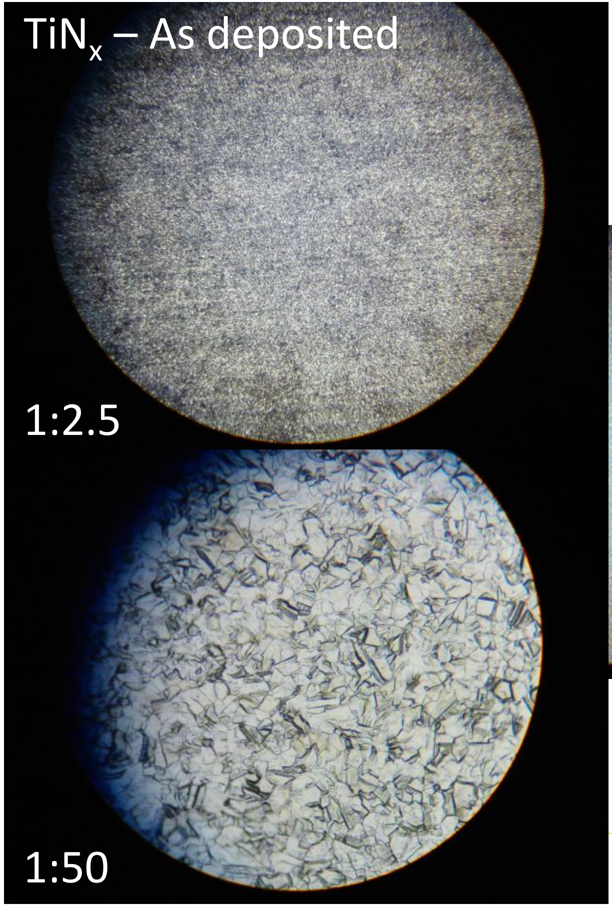
Sample	Post-treatment	Contact angle (DI H_2O)
Uncoated 304L	-	65°
TiN_x	-	0°
$Ti(Al)C_x$	-	45°
$Ti(Al)N_xC_y$	-	28°
TiN_x	O_2 plasma	0°
$Ti(Al)C_x$	O_2 plasma	0°
$Ti(Al)N_xC_y$	O_2 plasma	0°

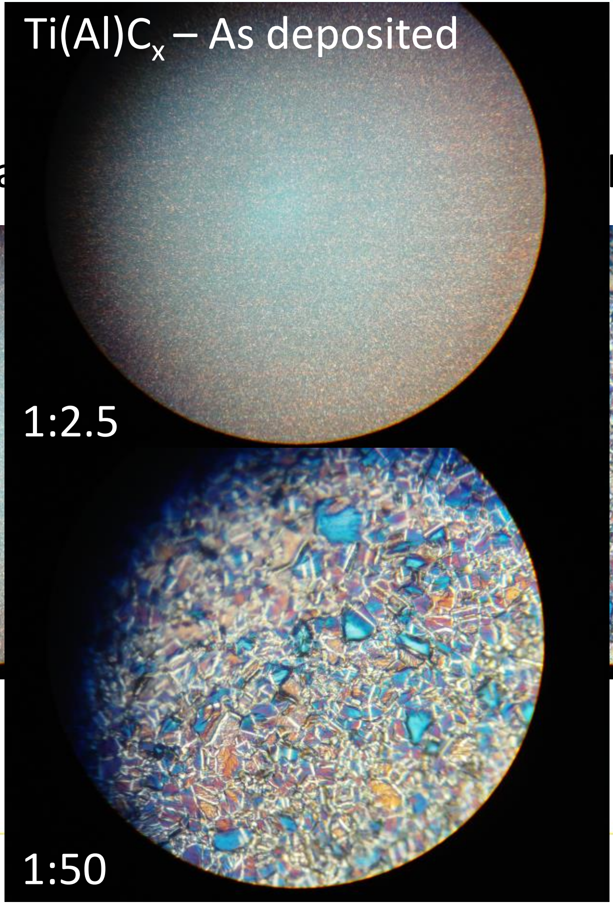
TiN_x, $Ti(Al)C_x$ and $Ti(Al)N_xC_y$ – Corrosion

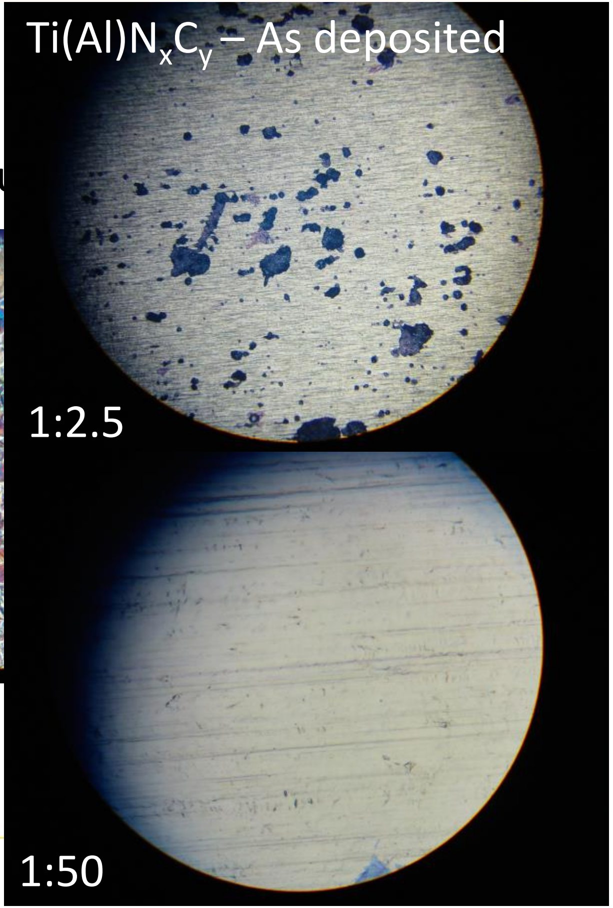
- 10% HCl @ 22 °C

Sample	Post-treatment	Corrosion rate / mm/year
Uncoated 304L	-	0.63
TiN_x	-	0.48
$Ti(Al)C_x$	-	0.50
$Ti(Al)N_xC_y$	-	0.12
TiN_x	O_2 plasma	0.59
$Ti(Al)C_x$	O_2 plasma	0.30
$Ti(Al)N_xC_y$	O_2 plasma	0.10

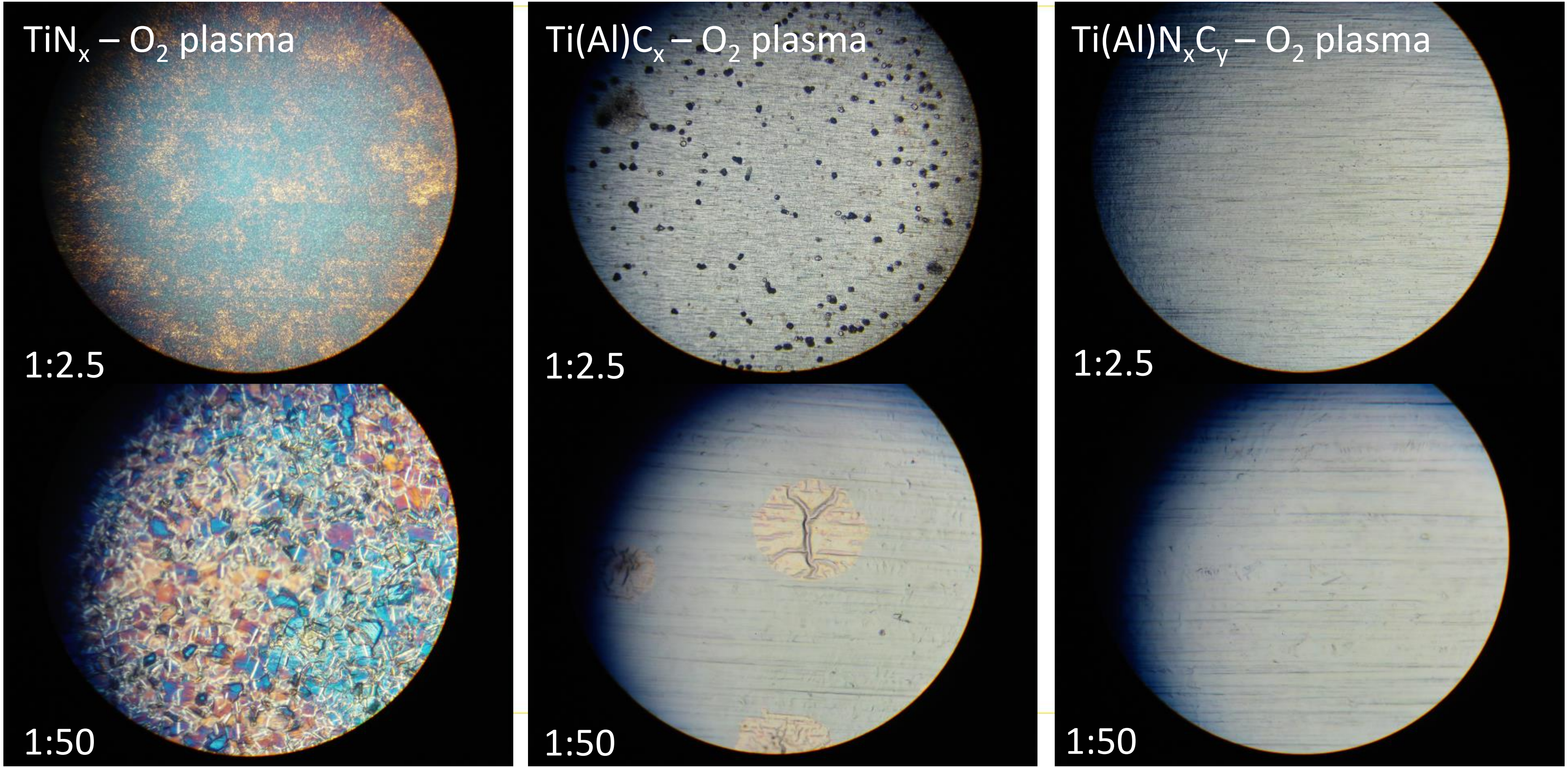
TiN_x, $Ti(Al)C_x$ and $Ti(Al)N_xC_y$ – Corrosion





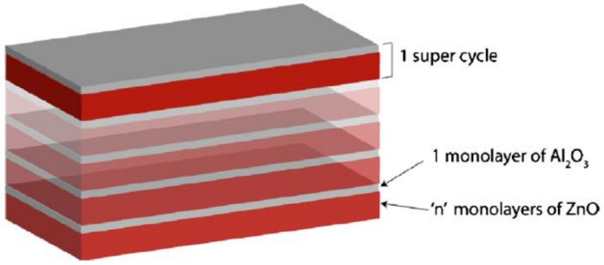


TiN_x, $Ti(Al)C_x$ and $Ti(Al)N_xC_y$ – Corrosion



Case II

- Al doped ZnO
  - Transparent n-type semiconductor
  - ALD film growth
    - Al_2O_3 deposited from trimethyl aluminium (TMA) and H_2O
    - ZnO deposited from diethyl zinc (DEZ) and H_2O
    - Deposition temperature 225 °C
  - Different concentrations of Al was doped into ZnO
    - Pure ZnO
    - AZO 49:1 (49 × ZnO + 1 × Al_2O_3)
    - AZO 24:1 (24 × ZnO + 1 × Al_2O_3)
    - AZO 12:1 (12 × ZnO + 1 × Al_2O_3)
    - Pure Al_2O_3



P. Bajernee at al., J. Appl. Phys. 108 (2010) 043504.

Al:ZnO – Refractive index

- The composition can be digitally controlled

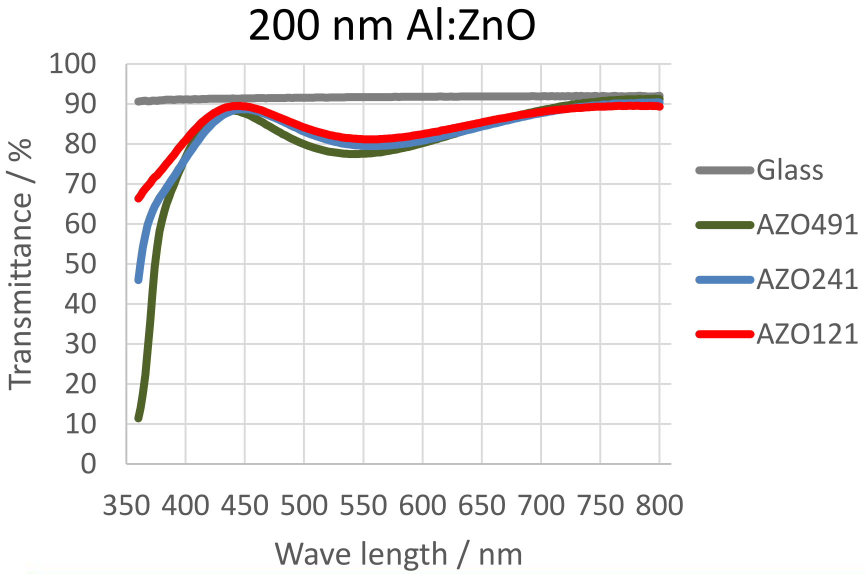
TABLE I. List of samples used for obtaining data showing the ratio of Zn to Al cycles used to obtain various Al doping concentration. Here, n is the number of DEZ-DI water cycles inserted between consecutive TMA-DI water cycles. This constitutes a single supercycle. By repeating the supercycles, estimated total thickness is obtained. The true total thickness is based on measurement using spectroscopic ellipsometry. The estimated at. % Al is calculated by the method shown in text. The true at. % Al doping is obtained via EDX.

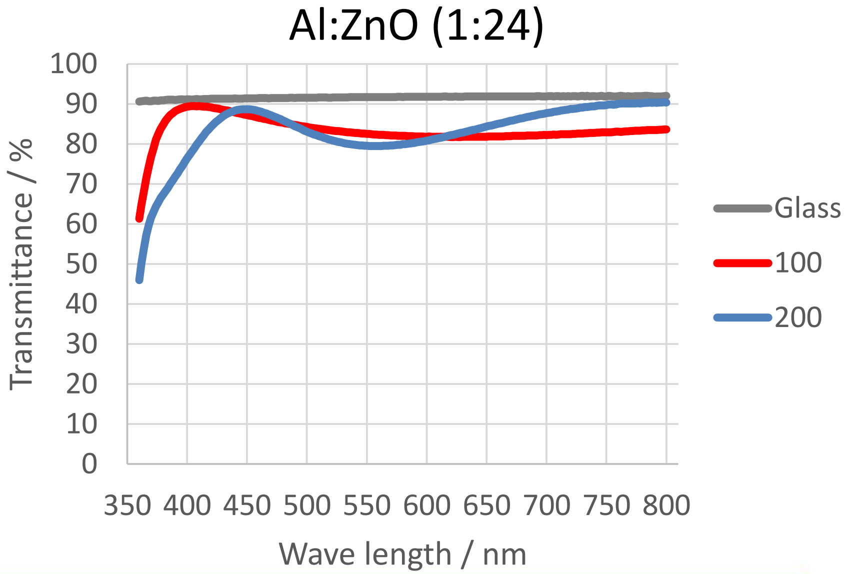
Sample	n	Thickness of one supercycle (nm)	Total number of supercycles	Estimated total thickness (nm)	True total thickness (nm)	Estimated Al (at. %)	True at. % Al (via EDX)
ZnO	N/A	N/A	N/A	100.0	103.0	0	0
Zn:Al=40:1	40	8.1	12	97.2	101.0	1.2	1.5
Zn:Al=20:1	20	4.1	24	98.4	97.3	2.4	3.0
Zn:Al=13:1	13	2.7	37	99.9	95.0	3.7	7.3
Zn:Al=10:1	10	2.1	48	100.8	96.8	4.8	8.1
Zn:Al=8:1	8	1.7	59	100.3	96.8	5.9	10.9
Zn:Al=6:1	6	1.3	77	100.1	89.1	7.7	17.3
Zn:Al=5:1	5	1.1	91	100.1	86.3	9.1	24.6

P. Bajernee at al., J. Appl. Phys. 108 (2010) 043504.

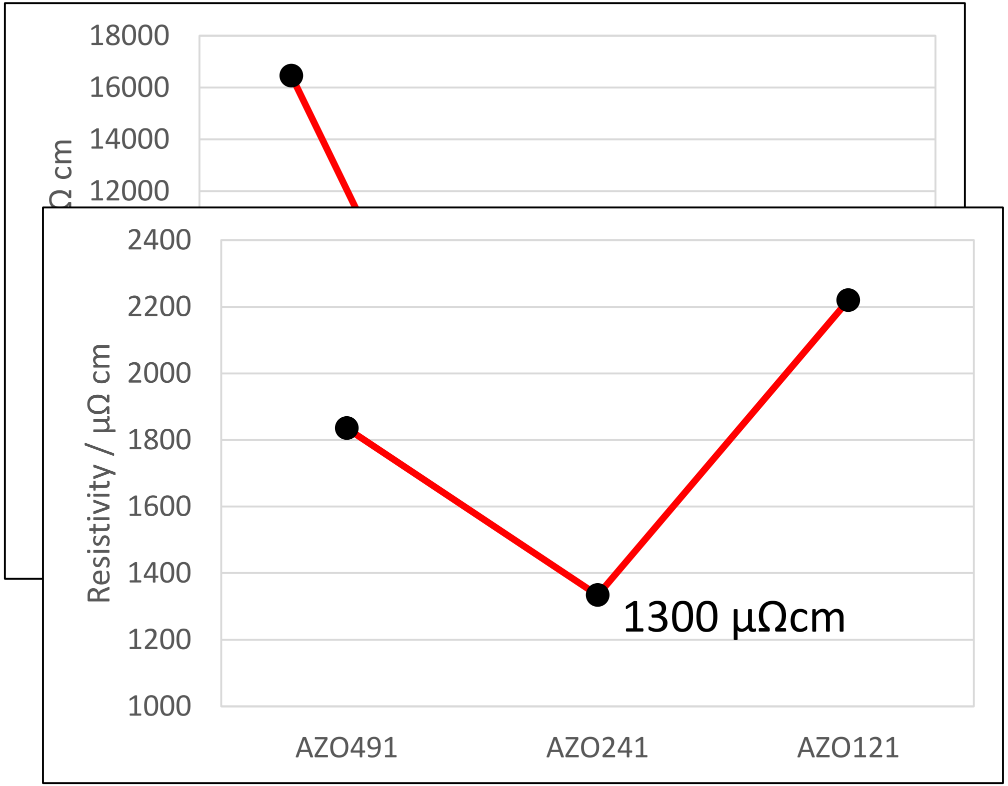
Al:ZnO – Transmission

- The films have over 80 % transmission in the visible range
- The unique properties of ALD can be utilized to model a thickness giving the optimized transmission





Al:ZnO – Electrical resistance



- Doping with Al greatly improves the conductivity of ZnO
  - Donor electrons
- An optimum is achieved at pulsing ratio 24:1
  - Too much Al resulted in insulating Al_2O_3 clusters

Conclusions

- Atomic layer deposition is a versatile tool for precision coating
- ALD TiN_x, $Ti(Al)C_x$ and $Ti(Al)N_xC_y$ coatings can be used to protect stainless steel
  - $Ti(Al)N_xC_y$ gives the best performance
- ALD enables control over Al doping into ZnO thin films
  - Lowest resisitivity is achieved with 24:1 Zn:Al pulsing ratio
  - Transmission over 80 % over the visible range

Thank you

www.beneq.com
emma.salmi@beneq.com

Beneq