



Direct-write ALD of In₂O₃:H and ZnO at the micro- and nanoscale

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Abstract

We demonstrate area-selective ALD (AS-ALD) of transparent conductive oxides at both the microscale $(In_2O_3:H)^1$ and at the nanoscale (ZnO).

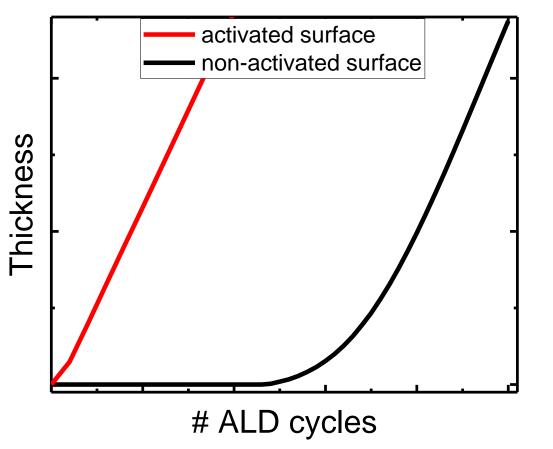
Since no subtractive steps are used to pattern H-terminated Si (10 nm a-Si:H) we refer to these processes as *direct write* ALD.

An O₂ fed µ-plasma printer or an electron beam induced deposition (EBID) of a SiO₂ seed layer are used to activate the surface for the subsequent thermal ALD.

Nucleation delay

Microscale In₂O₃:H

A nucleation delay is observed on a-Si:H for thermal S ALD of In_2O_3 :H and In_2O_3 :H exploited for AS-ALD.



Methods

- Local substrate activation is obtained using an O₂ fed μ-plasma printer² for microscale dimensions.
- SiO₂ EBID seed layer (TEOS + H₂O) are used to activate the surface for nanoscale dimensions

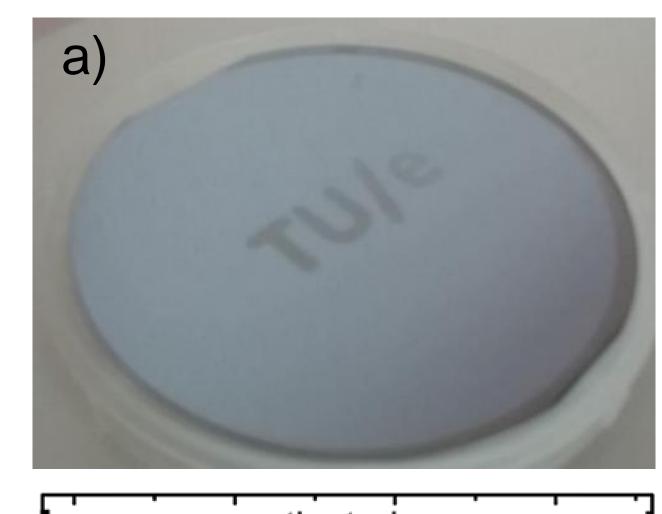
1st ALD cycle

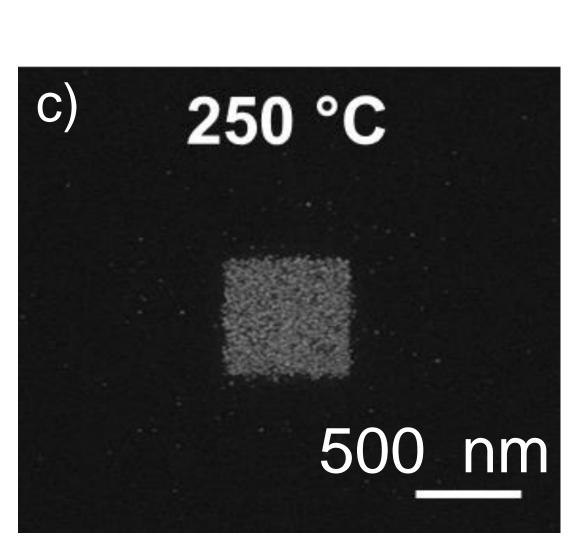
2) Building step Area-selective ALD Pulse A Pulse B Pulse B

letters TU/e created using the µ-plasma printer to locally activate the surface and 400 ALD cycles of In₂O₃:H

wafer with the

b) XPS In3d doublet on the activated (black) and non-activated area (red)





1) Patterning step

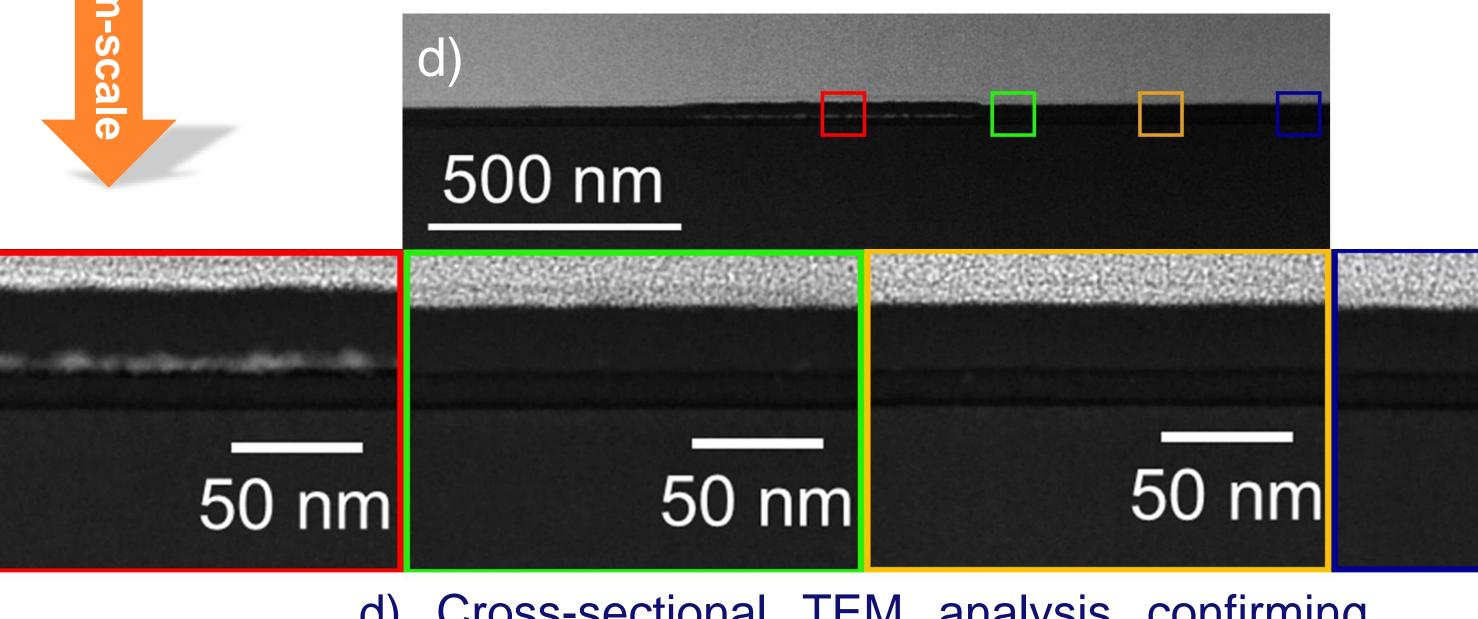
modification deposition

by μ-plasma / by EBID

µm-scale / nm-scale

Surface | Seed layer

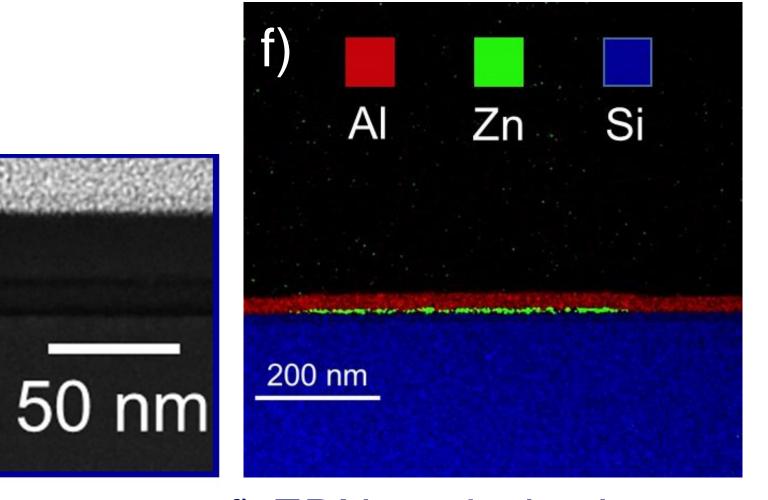
c) Top-view SEM of ZnO AS-ALD on an ultrathin ~1 nm EBID SiO₂ seed-layer



nth ALD cycle

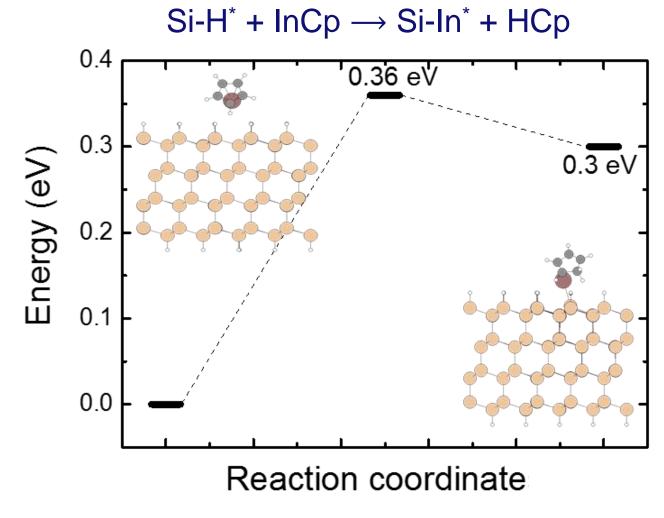
d) Cross-sectional TEM analysis confirming robust selectivity after 80 ALD cycles at 250 °C. High magnification TEM for different locations

Nanoscale ZnO

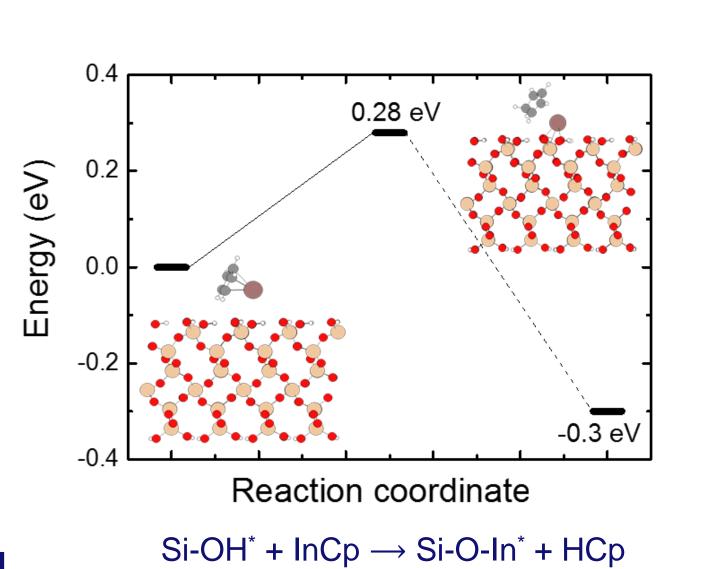


f) EDX analysis shows no ZnO deposition outside the patterned area

Underlying Surface Chemistry as Calculated by Density Functional Theory (DFT)



Thermodynamically hindered



Si-H* + $Zn(CH_2CH_3)_2 \rightarrow Si-Zn-CH_2CH_3^* + C_2H_6$ 1.5

1.0

0.5

0.0

-0.026 eV

PEZ on H-terminated Si

Reaction coordinate

-0.047 eV
-1.0
-1.5
-DEZ on OH-terminated Si

Reaction coordinate

Kinetically hindered

 $Si-OH^* + Zn(CH_2CH_3)_2 \rightarrow Si-O-Zn-CH_2CH_3^* + C_2H_6$

[1] A. Mameli, et al., Chem. Mater., **29**, 921-925 (2017) [2] J. R. G. Schalken et al., Nanoscience Nanotechnol. Letters **7**, 62-66 (2015)