# Characterisation of TCO-Si interfaces with XPS, HREM and ab-initio modelling based on DFT

S. Diplas

*Research Team: Material Physics*

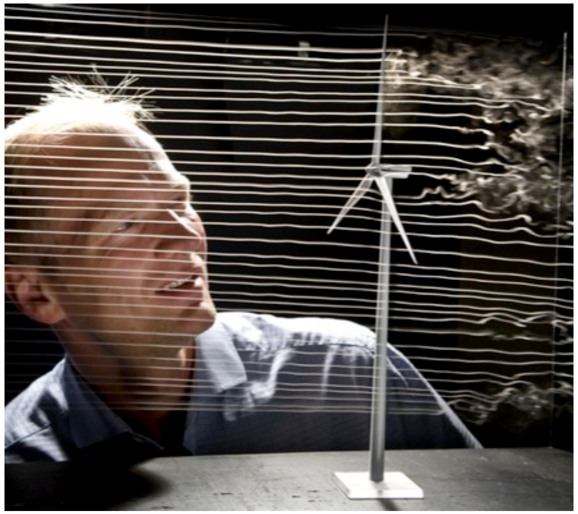
*Department: Synthesis & Properties*

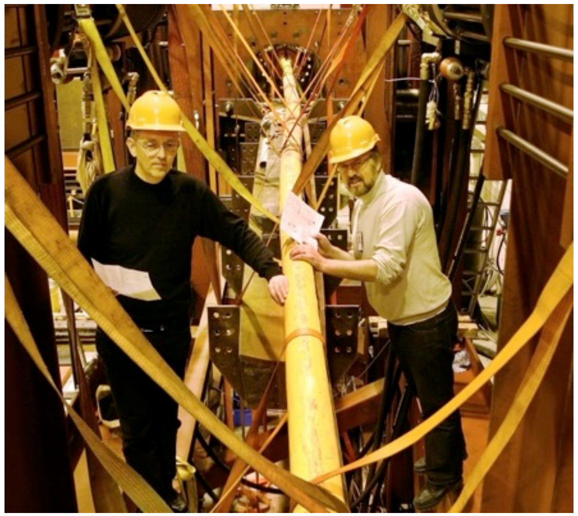
*SINTEF Materials and Chemistry, Forskningsvn 1, NO-0314 Oslo, Norway*
*www.sintef.no*

*spyros.diplas@sintef.no*
*Tel:+4798230427*

# SINTEF is the largest independent research organisation in Scandinavia

- Leading expertise in the natural science and technology, environment, health and social science
- 2,200 employees from 67 countries
- Annual sales of 350 mill euro – customers in 60 countries
- A non-commercial research foundation with subsidiaries





# A multidisciplinary research organisation with international top level expertise in specific fields

SINTEF Building and Infrastructure

SINTEF ICT

**SINTEF Materials and Chemistry**

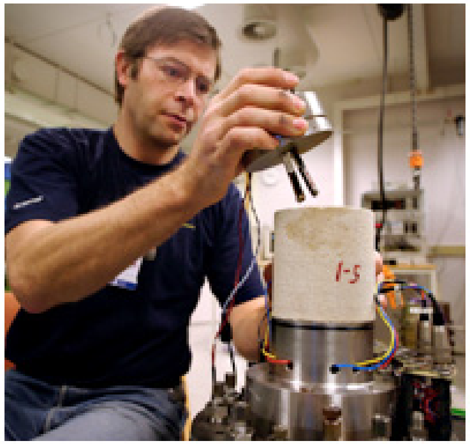
SINTEF Technology and Society

SINTEF Energy Research

SINTEF Fisheries and Aquaculture

SINTEF Petroleum Research

MARINTEK



# Our vision: Technology for a better society

## Our role

- Creating value by applying knowledge, research and innovation
- Delivering solutions for sustainable development
- Building and operating research laboratories
- Providing premises for social debate and policy decisions

# Outline

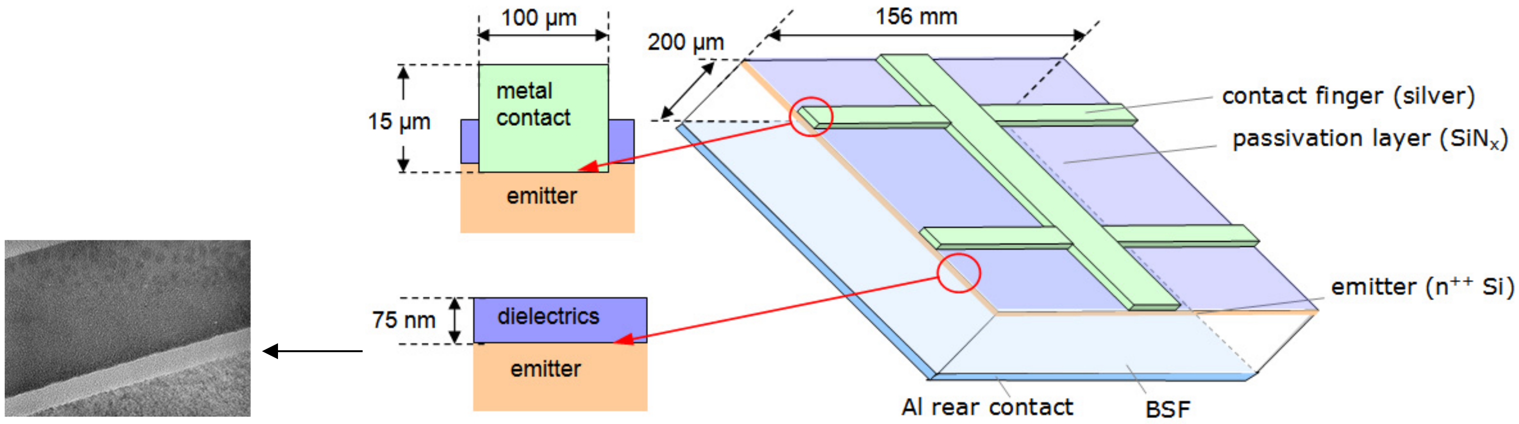
- Motivation
- Experimental details

-ZnO/Si

-ITO/Si

- Conclusions

# Motivation




- Two performance bottlenecks of current solar cells:
  - resistance at contacting interface
  - **recombination at passivation - semiconductor interface**

- The above processed processes are quantum mechanical by nature
  - first principles modelling is needed

## Magnetron Sputtered AZO:H

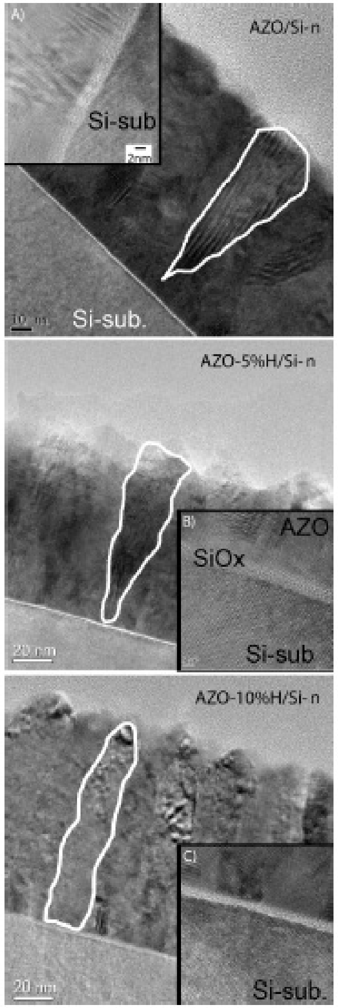
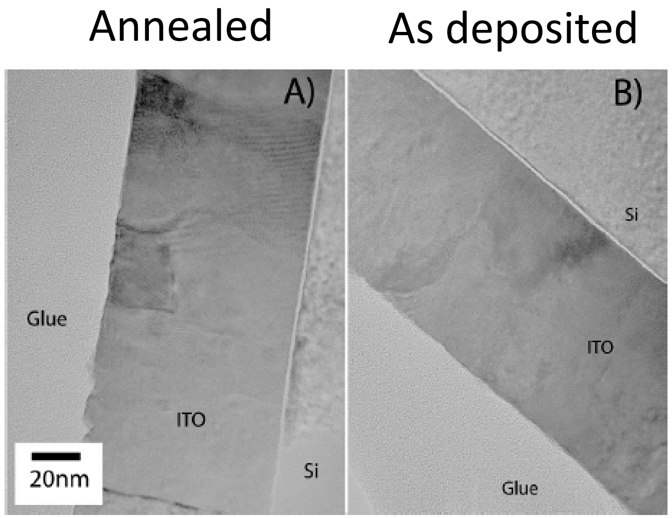



FIG. 2: TEM image of AZO/Si-n with A) no $H_2$, B) 5 $\%H_2$, and C) 10 $\%H_2$.

*A. Thøgersen. Submitted to J. Appl. Phys. (2012)*

## Magnetron Sputtered ITO

### Annealed / As deposited



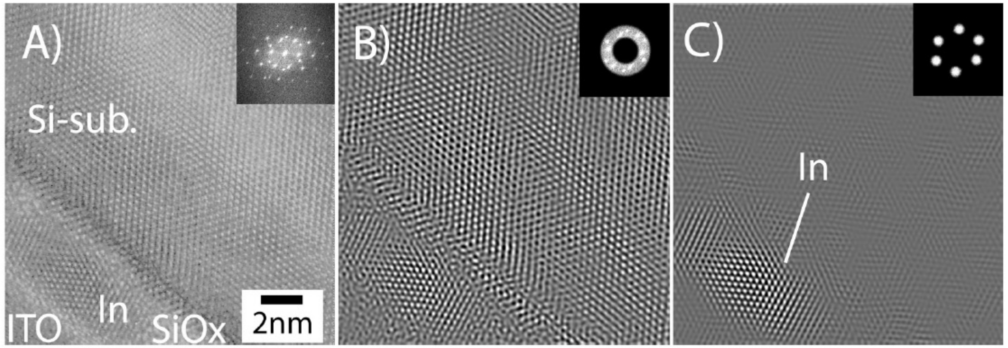
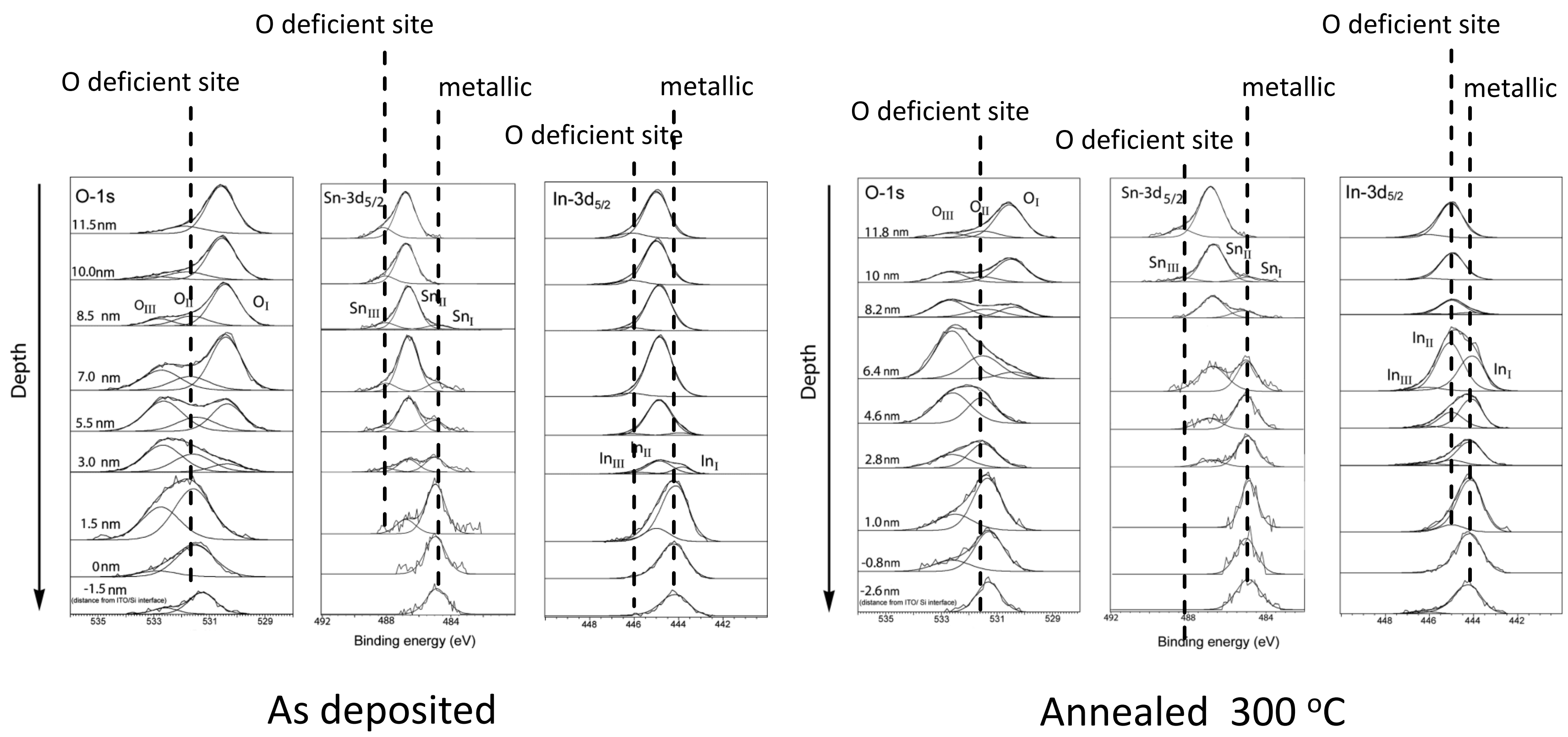




FIG. 10. HRTEM images of the Si substrate and the interface nanocrystal, where (A) is the HRTEM image, (B) is the HRTEM image after applying a circular mask, and (C) is after applying a mask of only the In diffraction pattern.

*Thøgersen, Rein, Monakhov, Mayandi and Diplas, J. Appl. Phys. 109, 113532 (2011)*

# XPS Depth profiles

Magnetron Sputtered ITO

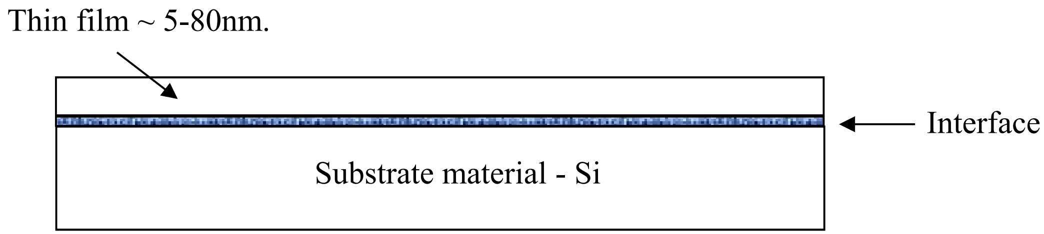



*Thøgersen, Rein, Monakhov, Mayandi and Diplas, J. Appl. Phys. 109, 113532 (2011)*

# Approach

1. Near in-situ XPS upon deposition of ITO on Si

2. Preparation of model interfaces of ITO-Si and ZnO-Si with thin film deposition techniques (pulsed lazer deposition, electron beam deposition) and subsequent post-deposition treatments (air annealing at 300 °C).




3. Advanced characterisation: x-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (HRTEM/STEM)

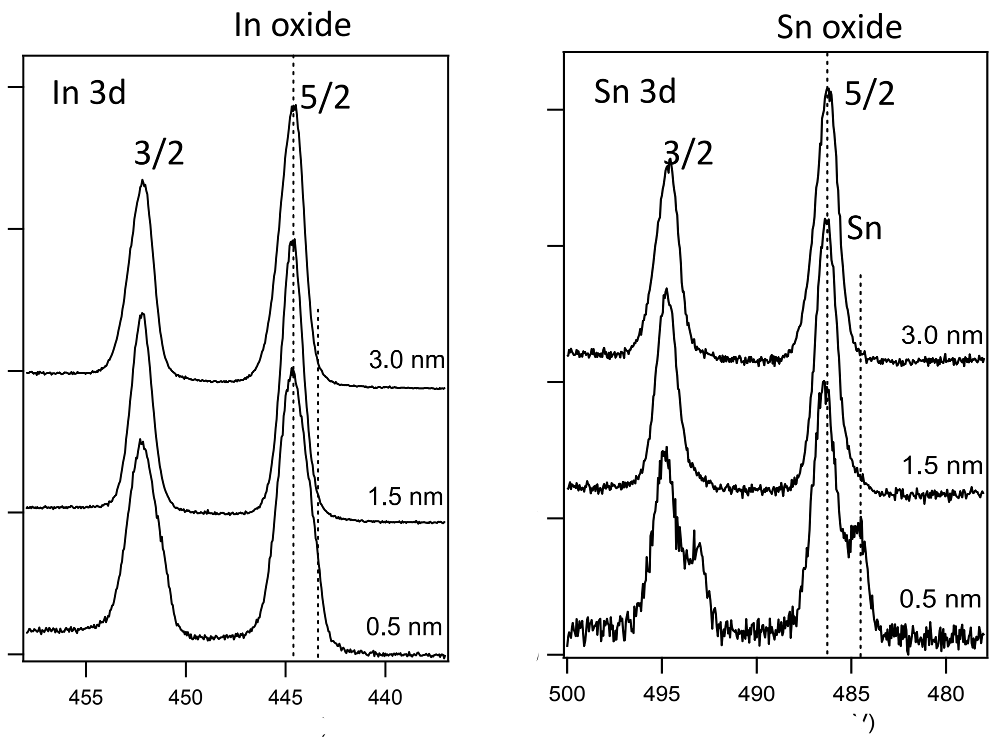
4. Performance of DFT based MD for bonding and atomistic structures

# Result 1: Pure In and Sn form at the ITO-Si interface during early stages of deposition

## Practical significance:

In is an acceptor in Si, In doped thin subsurface layers at the ITO/n-Si interface form a shallow p+ emitter. This may explain why degenerate n-type ITO deposited on n-type Si can be used for fabrication of high-efficiency ITO/n-Si heterojunction solar cells.

# Background for result 1
# Near in-situ XPS upon deposition of ITO on n-a-Si



Production of thin (3nm) and thick films (70 nm) on:
a-Si, p-type (001), n-type (001), n-type (111) Si
treated in HF solution

## ITO/a-Si and c-Si (e-beam)

CVC SC-5000 chamber, Temescal STIH-270-1 e-beam gun
The ITO pellets were evaporated from a POCO graphite crucible (2-5 x $10^{-6}$ Torr).
Deposition @ RT and $0^o$ from the vertical axis

## ZnO and ZnO:Al on c-Si and a-Si (PLD).

KrF excimer laser at 248 nm wavelength (Lambda Physik LPX Pro 210i).
ZnO target (American Elements, 99.999%) was ablated with a laser fluency of 2-3 J/cm² at a pulse repetition rate of 2 Hz.
Vacuum chamber base pressure before deposition < 1 x $10^{-6}$ Torr.
Depositions @ RT or 500°C, in the $O_2$ remaining base pressure or in $10^{-3}$ Torr $O_2$.

**Films studied as deposited and after air annealing at 300 $^o$C for 30 mins**

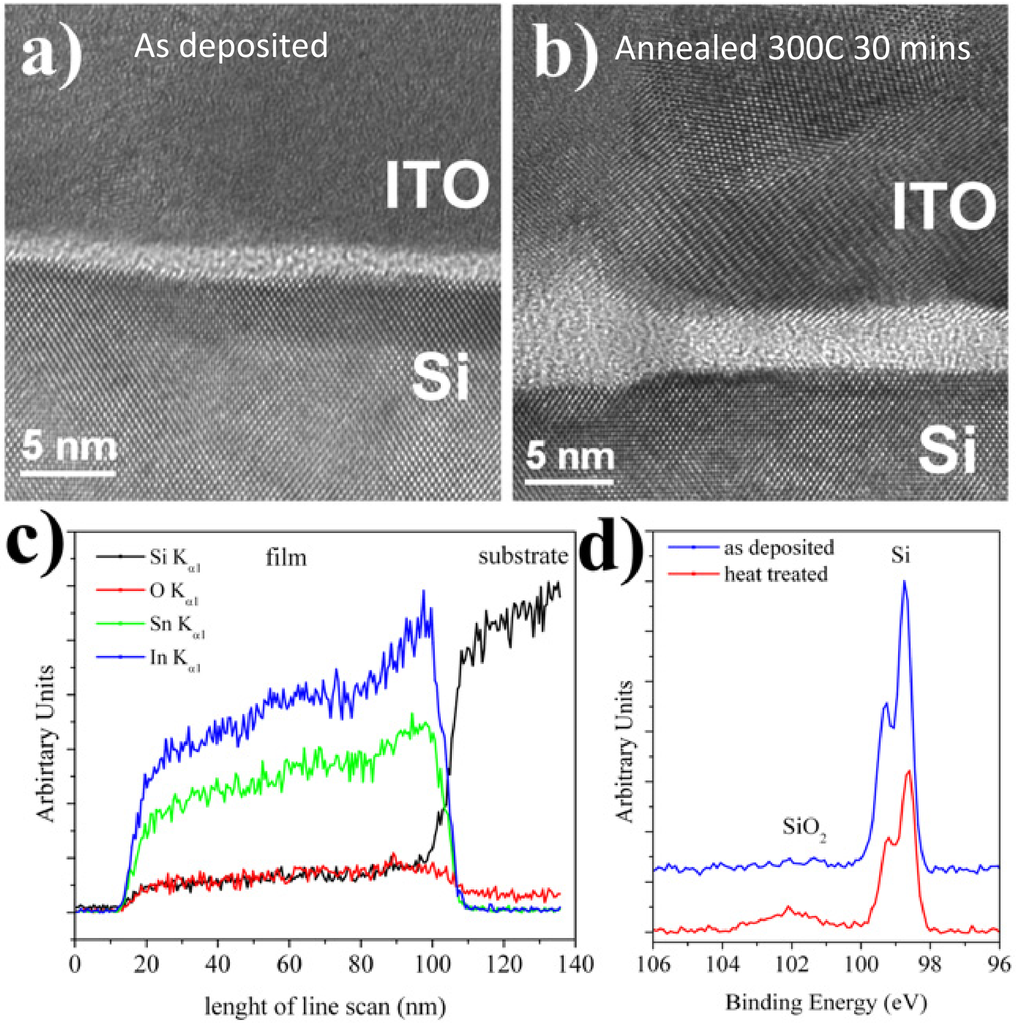
- **XPS** for thick and thin samples (KRATOS AXIS ULTRA$^{DLD}$)
- **TEM** on thick samples (Jeol 2010 F & Aberration Corrected STEM VGHB501)

Result 2: **The interfacial oxide in TCO-Si is amorphous and increases in thickness upon air annealing. In, Sn, Zn and Si coexist in the oxide. Differences in contrast, EDS analysis and electron spectroscopic imaging on the TEM show that the oxide is divided in a Zn-rich and a Si-rich region .**

## Practical significance:

Interfacial oxides in heterojunctions form metal-insulator-semiconductor (MIS) structures and affect/limit electrical conductivity and therefore the device performance. Increased thickness of insulating oxide would increase resistance in the MIS structure. Compositional effects in conductivity?

# Background for result 2:



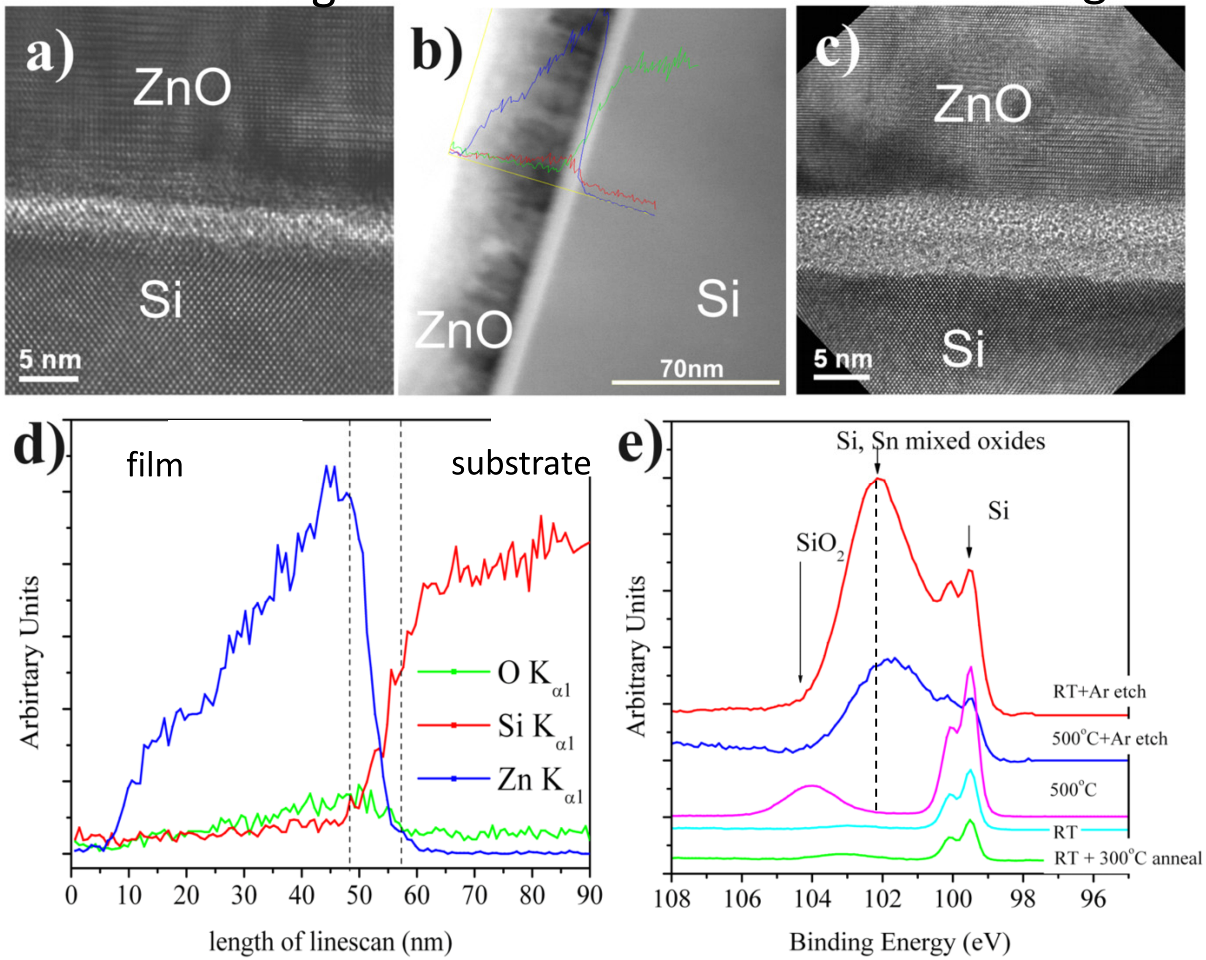

The interfacial oxide increases in thickness upon air annealing. In and Si coexist in the oxide

# Background for result 2:

Deposition at 500 C in $O_2$

No Ar etching

Ar etching

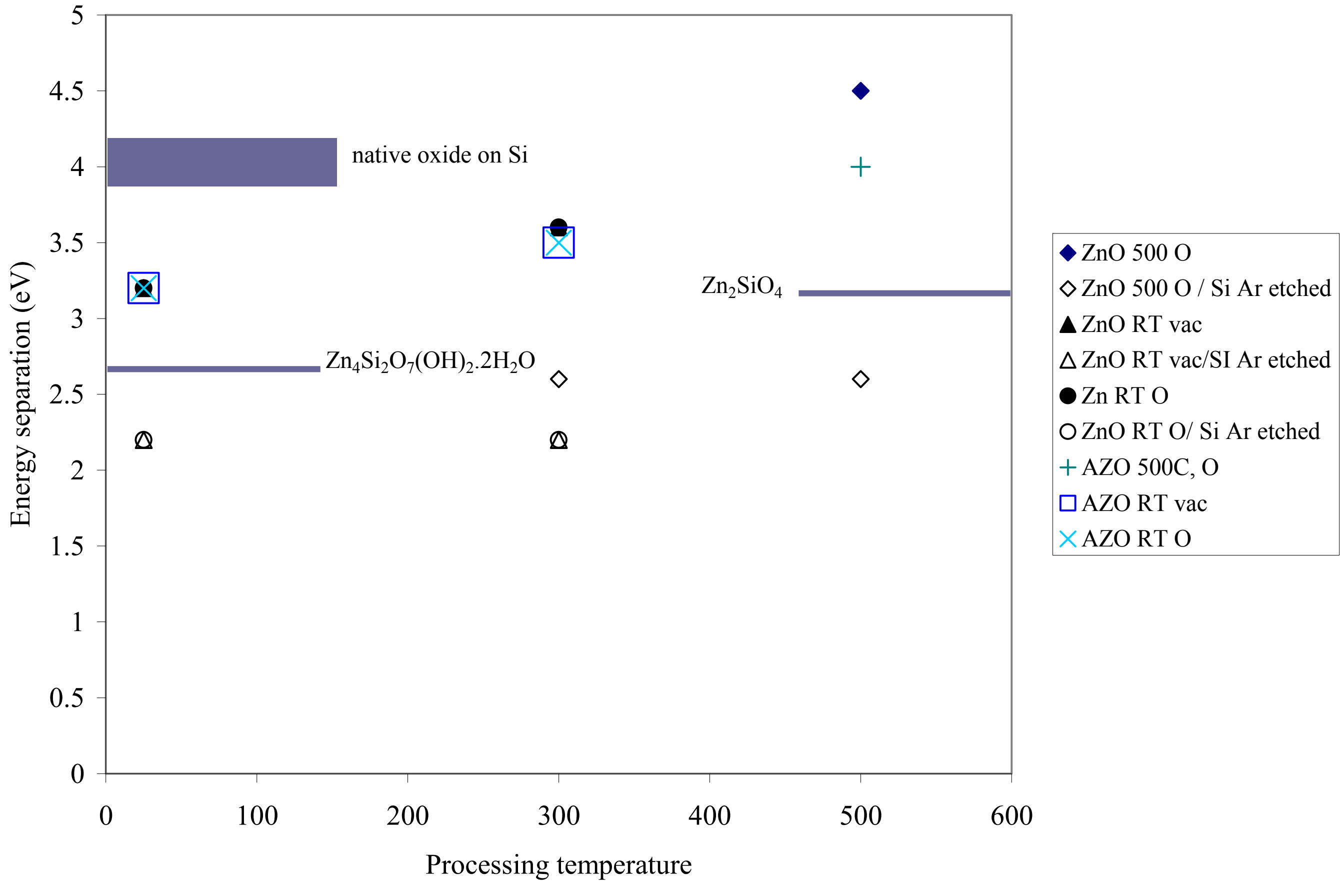


Result 3: Si chemical state at ITO-SI and ZnO-Si interface varies with processing but in most of the cases is less than 4+

Significance:

Presence of Si in the interfacial oxide in oxidation state less than 4+ can create fixed charges in the oxide.

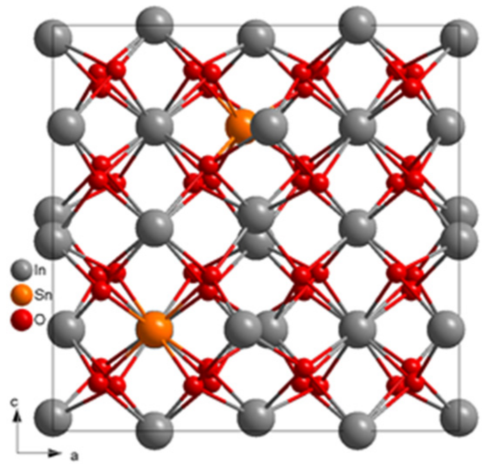
# Background for result 3 cont: Si-Si oxide separation for Si-ZnO interface



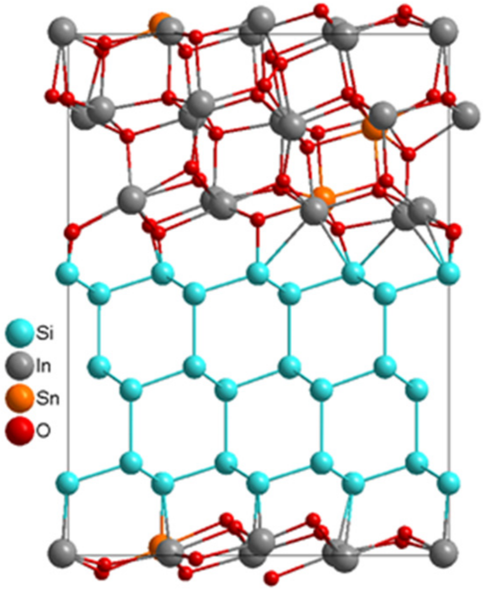

Deposition after Ar etching leads to interface oxide formation with a Si oxidation state between 2 and 3+. Vacuum annealing at 300 $^0$C for 30 mins does not alter this oxide

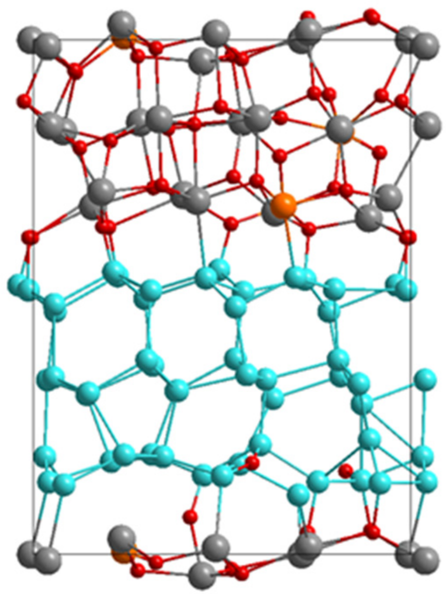
The ZnO/Si and AZO/Si interface after deposition at 500 $^o$C and $O_2$ consists of an oxide close to $SiO_2$ Deposition at RT form oxide with oxidation state closer to 3+. Annealing at 300 $^0$C for 30 mins does not lead to $SiO_2$ formation (oxidation state lower than 4+)

# Construction of model of ITO structure




The ITO model with 6.25 % Sn, that is with two Sn atoms per unit cell. In and Sn atoms are shown as large grey and yellow balls, while O atoms are shown as small, red balls.



The atomistic interface model between Si and ITO before (left) and after (right) a molecular dynamics calculation . The temperature was 1000 K, and 800 steps of 2.5 fs were performed. The vertical axis corresponds to the (111) axis of both Si and ITO. Si is represented as light blue balls,

# Concluding remarks

- The interfacial oxide between TCO-Si is influenced by:

-deposition temperature

-substrate surface condition

-post deposition treatment

- In and Zn coexist with Si in the interfacial ITO-Si and ZnO-Si oxides respectively.
- Metallic In and Sn coexist with the oxides at the ITO-Si interface
- Tuning of the thickness and composition of the oxide could be challenging and important in PV technology

# Acknowledgements

Heidi Nordmark

Alexander Ulyashin

Cecile Ladam

Annett Thøgersen

Frode Tyholdt

*John C. Walmsley*

Ole Martin Løvvik

SINTEF

Technology for a better society