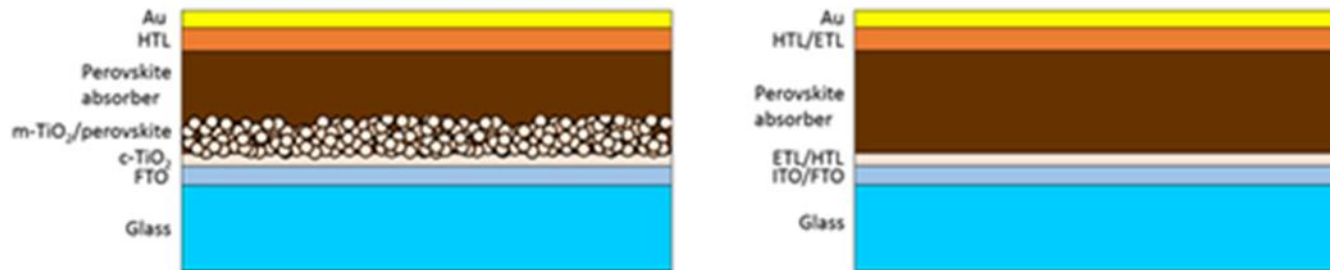


# IN-LINE DEPOSITION OF $\text{TiO}_{2-x}$ ELECTRON TRANSPORT LAYERS FOR LARGE AREA PEROVSKITE SOLAR CELLS

**John L. Hodgkinson**

# Motivation for Work



- Perovskite solar cells have shown considerable promise as architecture for the next generation of solar modules
- Challenge – cost effective large scale production
  - Typically spin coating / vacuum based technologies
  - Salford CVD optimise FTO / perovskite absorber
- In-Line deposition of compact TiO<sub>2-x</sub> ETL via AP PECVD
  - Advancement of this AP technology to achieve film properties and uniformity down to ~ 40 nm
  - Compatible with the online production of TCO
- Mesoporous cells constructed to evaluate ETL performance compared to a reference sputtered ETL

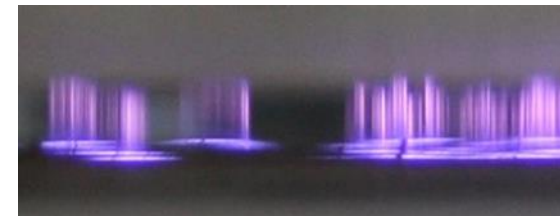
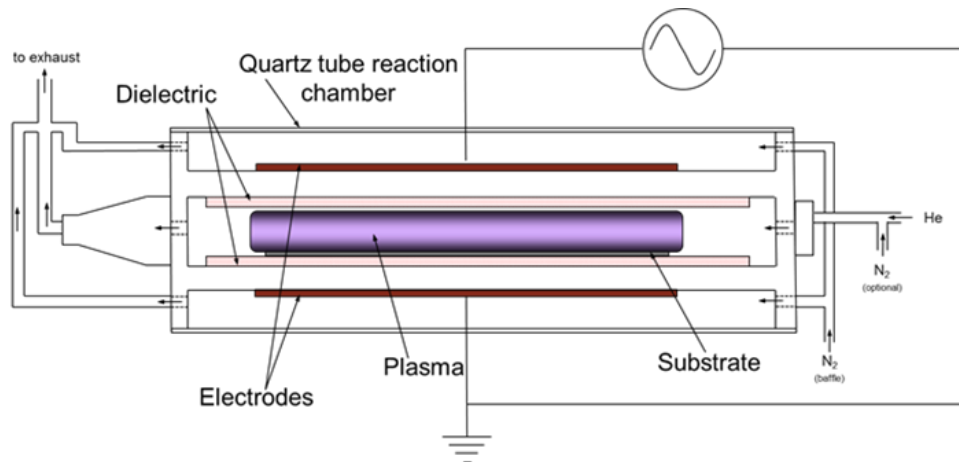
# Technical Approach

- APCVD is a cost effective industrial process
  - Continuous film growth on large area substrates
  - Deposit FTO on-line
  - Advantage for ETL process
- CVD provides control of film properties
  - Crystallinity
  - Topography
  - Stoichiometry
- Activated processes allow reduced substrate temperatures
  - Plasma (PECVD), Flame, Hotwire etc
  - Further opportunities for control
- PECVD typically operates under vacuum
  - Stable low temperature 'glow discharge'
  - Diffusion driven processes give conformal high quality films

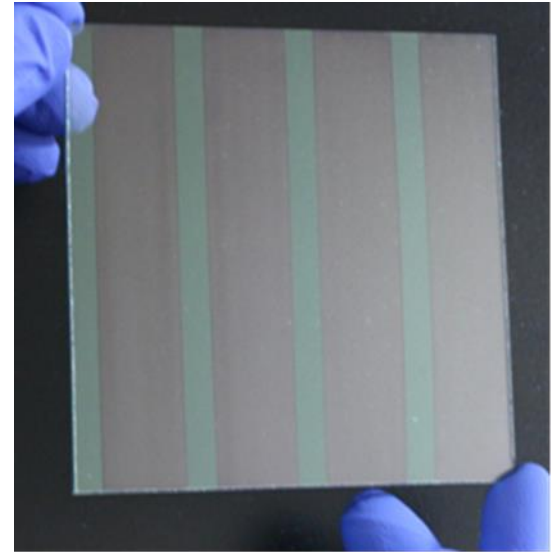
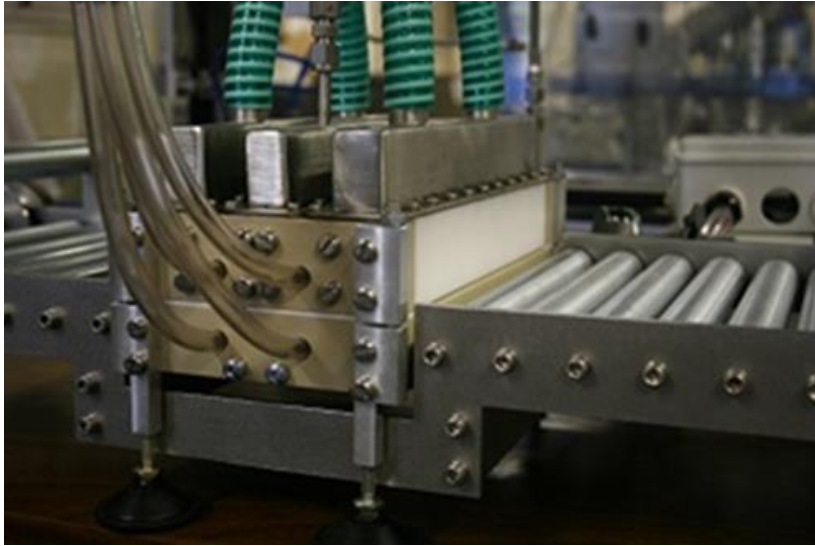


# Atmospheric Pressure Plasma Enhanced CVD

- AP plasmas typically operate close to thermal equilibrium
  - E.g. RF ICP, metal cutting, arc-jet plasma spray
- Barrier discharge systems provide non thermal plasma at AP
  - Controlled reaction of precursors for film growth
  - Deposition on thermally sensitive substrates
- Development can produce diffuse discharges & CVD
- Typically used for surface treatment & polymers due to reduced plasma stability and film quality
- Optimised system can provide device quality films at AP & RT!

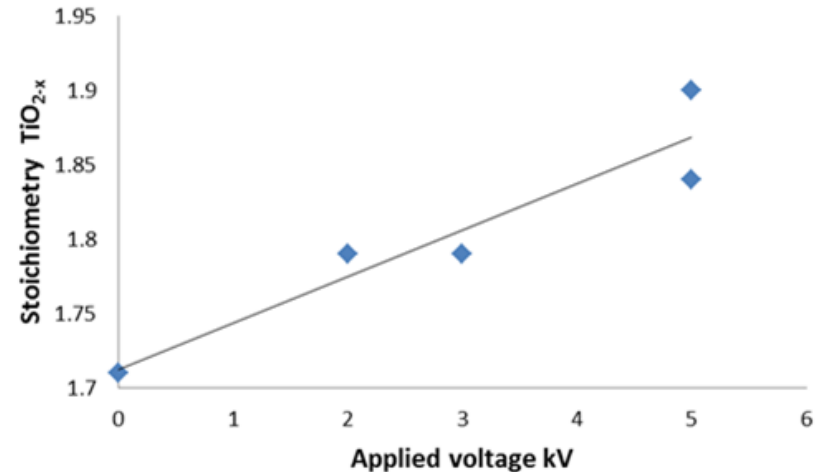
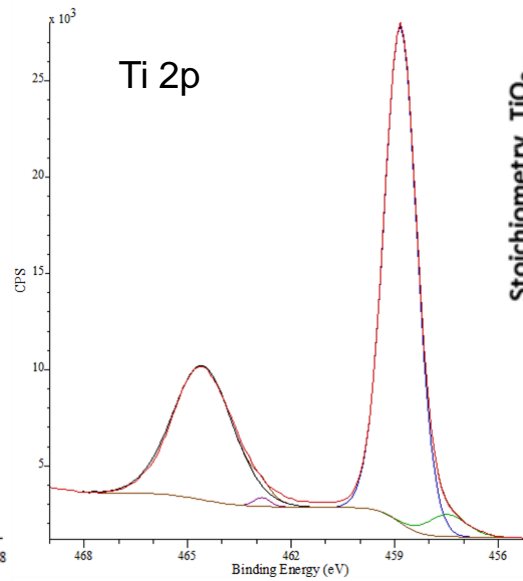
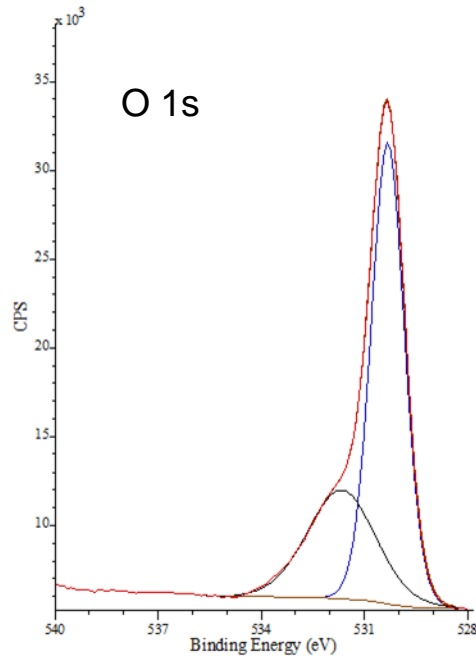


# Process Demonstrator



- Dual flow AP PECVD roll to roll system
- Convey solid substrates up to 20 x 20 cm
- Continuous film growth with high uniformity
- $\text{TiO}_{2-x}$  deposited from TTIP on 10 x 10 cm Solaronix TCO22-15, 10.7 m.hr<sup>-1</sup>
- 4, 6 & 8 passes resulted in 40 nm, 55 nm & 85 nm films
- Argon plasma, nitrogen under investigation

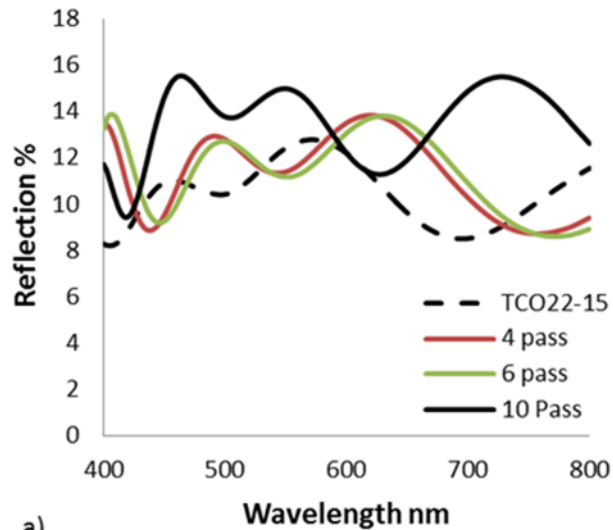
# Control of Film Properties



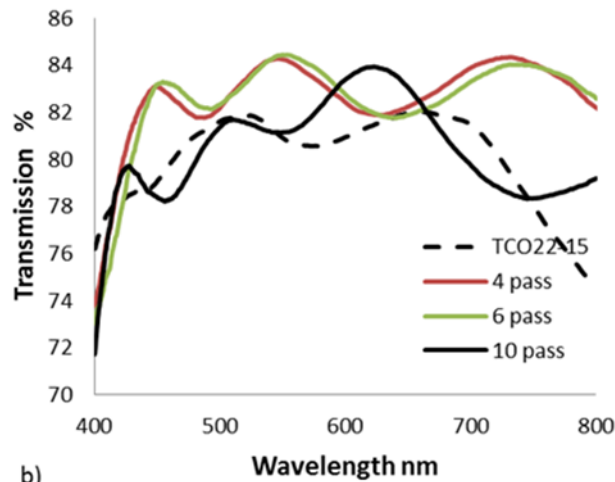
- XPS shows sub-stoichiometric titania
- Strong correlation between voltage and Ti:O ratio
- Films could be soft, hard or powdery dependant on plasma conditions
- Conditions chosen to provide dense, adherent powder free films

# Optical Properties

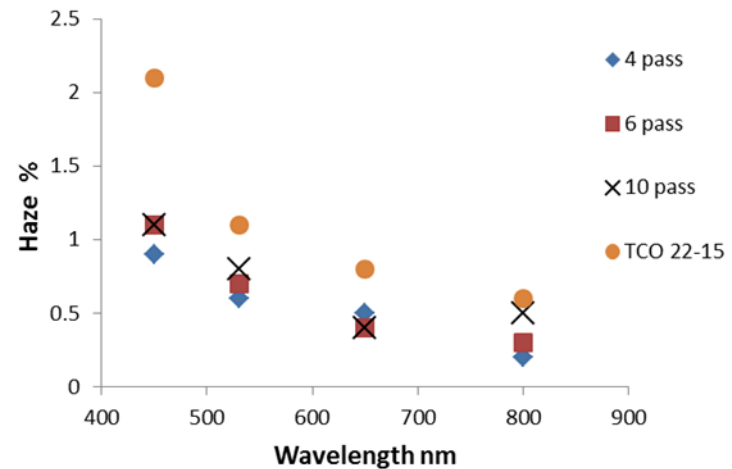
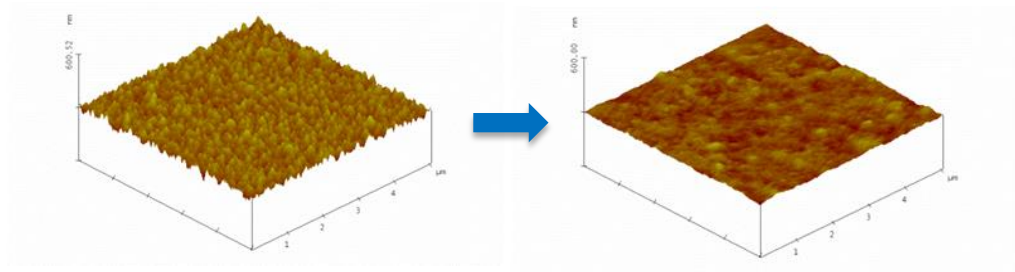
- $\text{TiO}_{2-x}$  increased mean reflection from 10 to 14 %
- Transmission increase from 80.0 % to  $82 \pm 1$  %
- Explained by a reduction in haze and hence net reduction in reflection due to smoother surface (14 to 4 nm RMS)



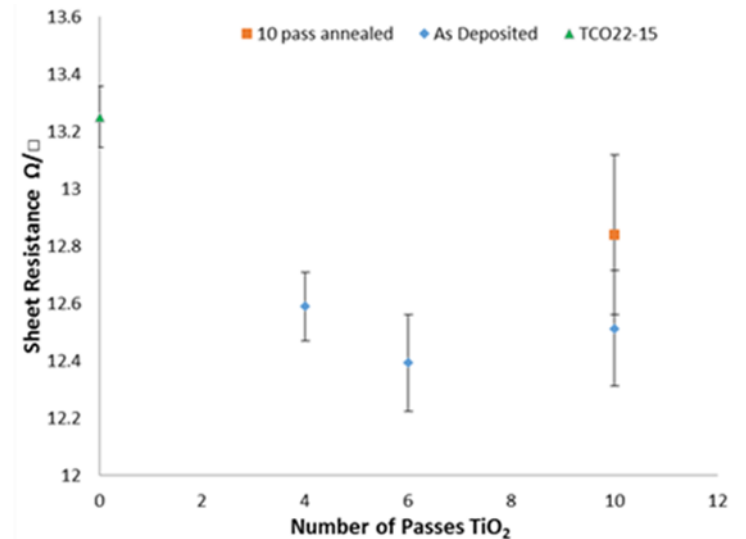
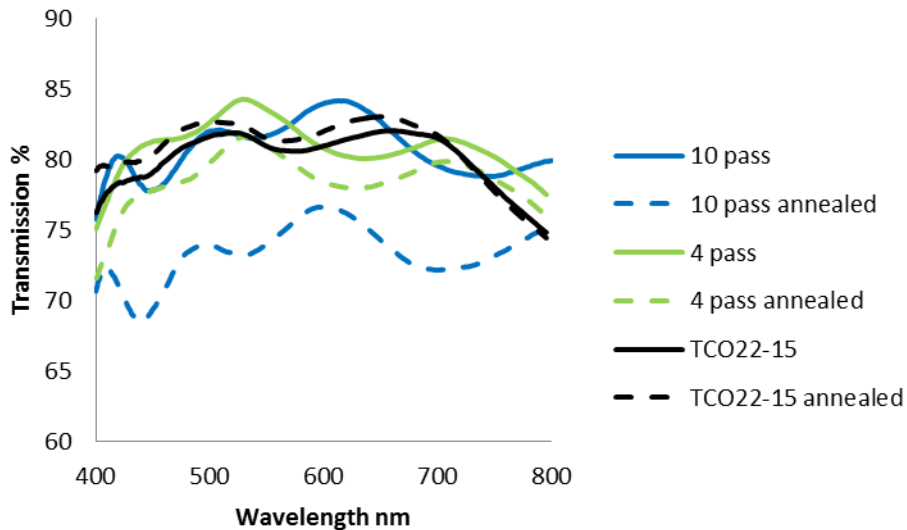
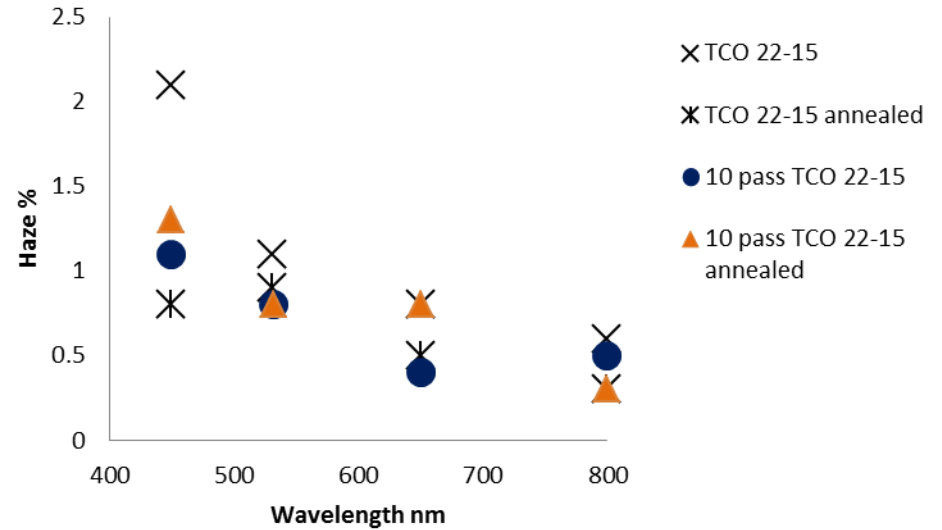
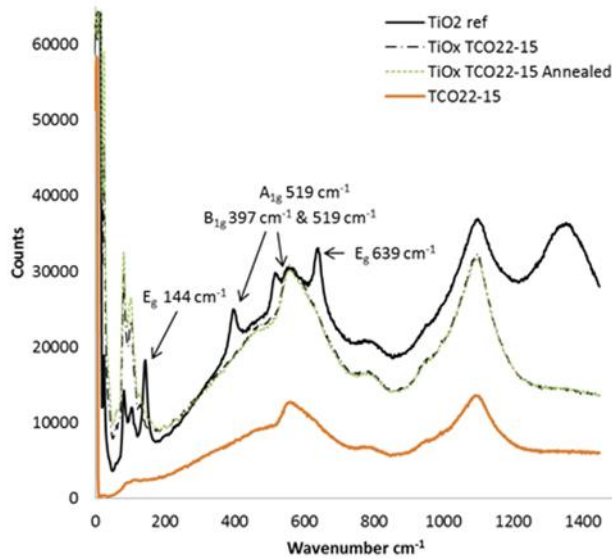
a)



b)

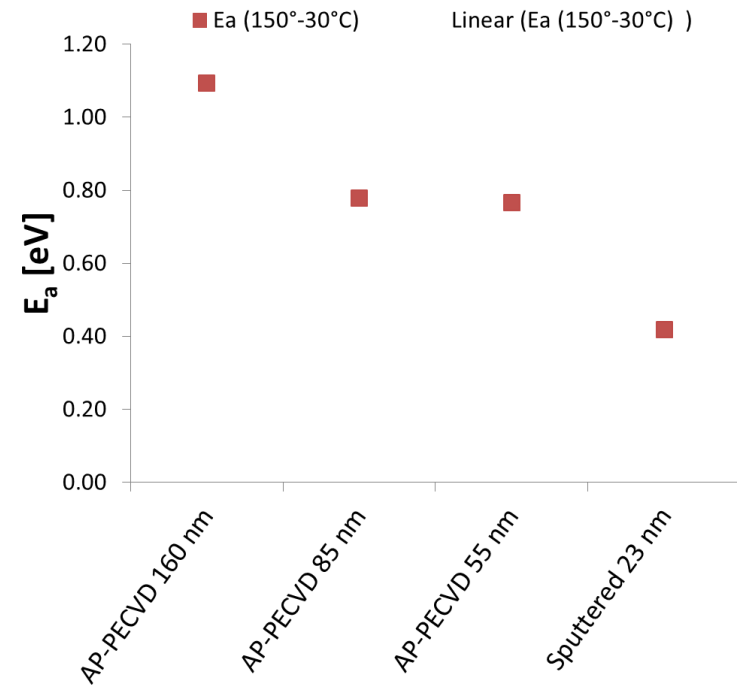
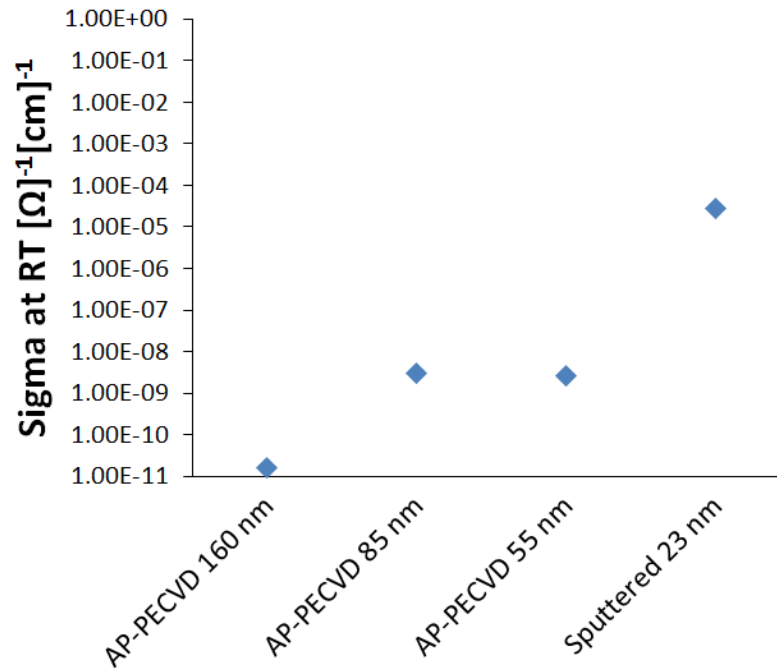


# Annealing Behaviour



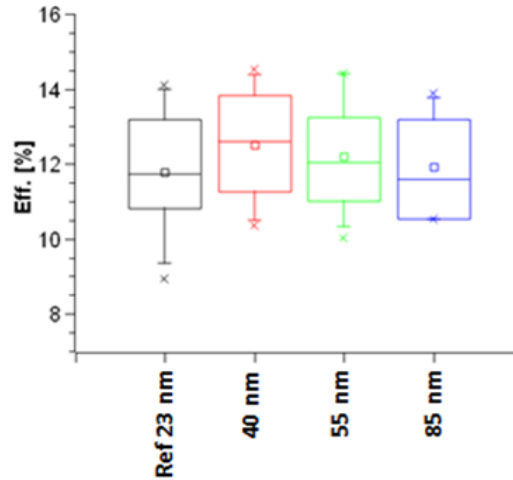
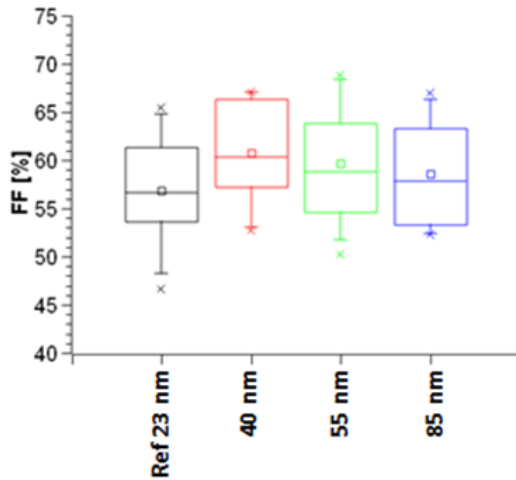
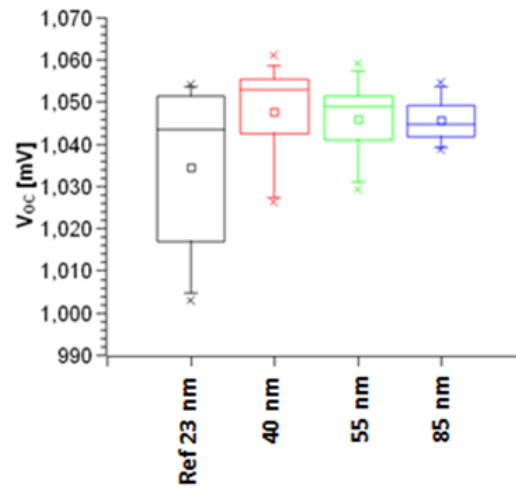
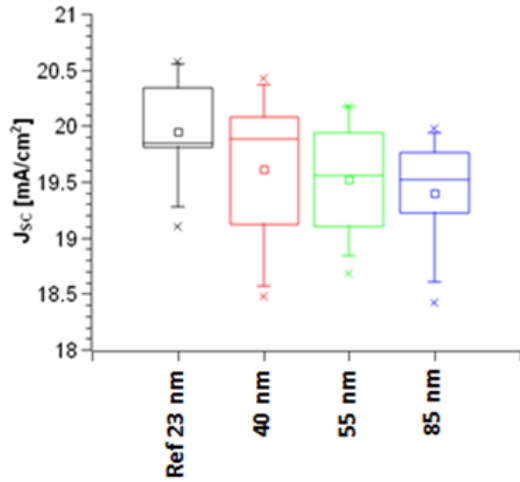


# Dark Conductivity



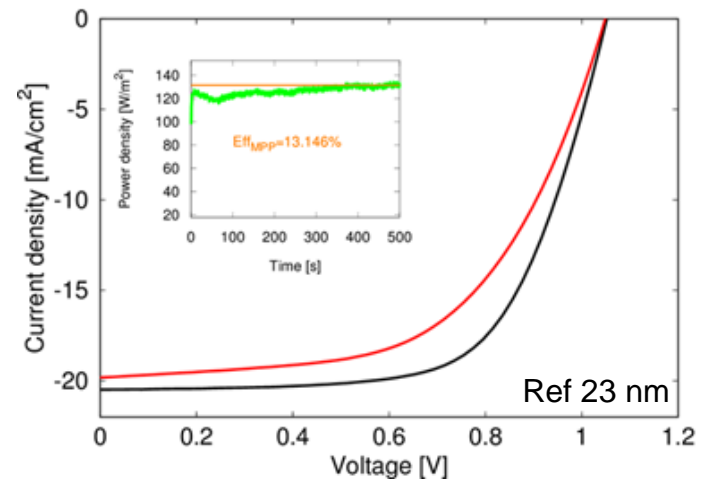
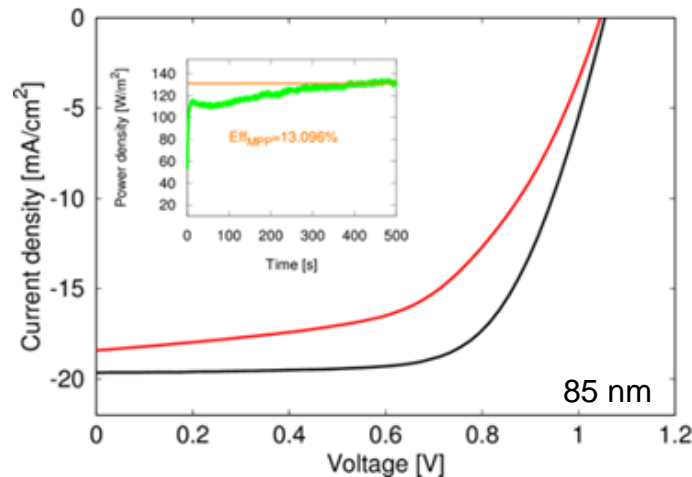
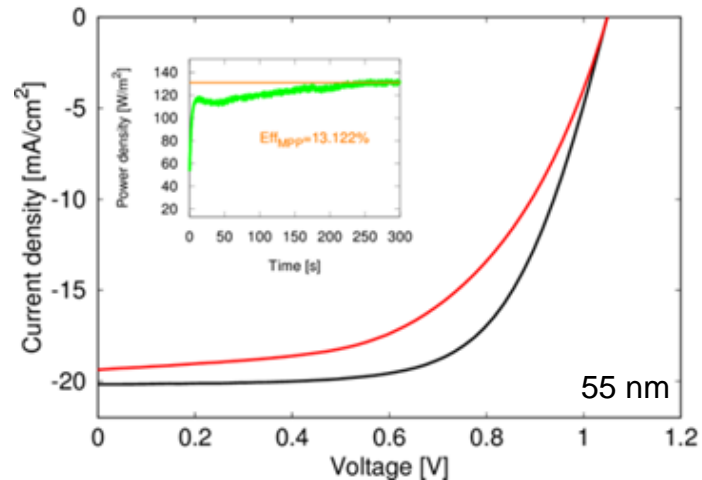
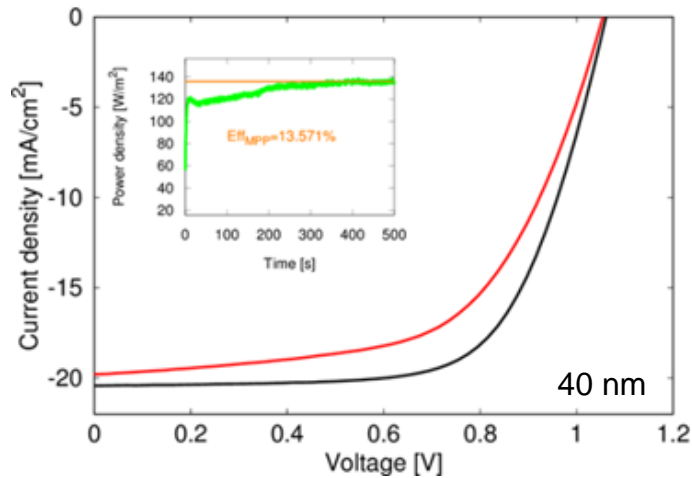
- $\sigma$  Dark &  $E_a$  measurements conducted for a range of  $\text{TiO}_{2-x}$  thicknesses on float glass
- Reduced conductivity compared to the reference
- Higher activation energy suggests less defective than the sputtered film
- Strong correlation with thickness

# Cell Results



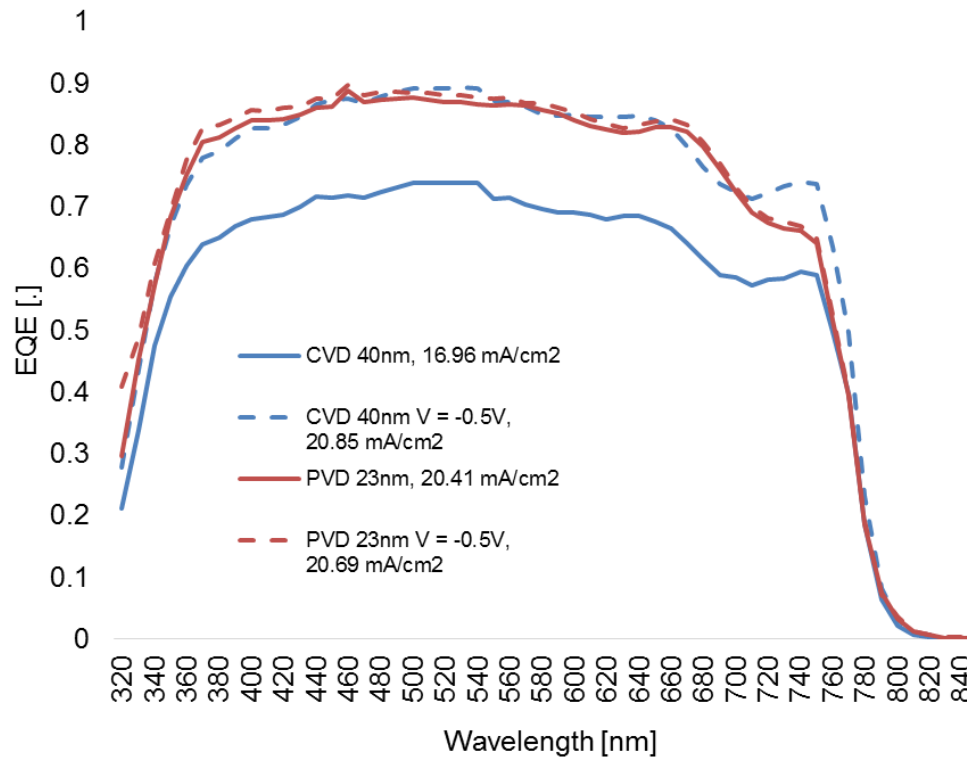
- TiO<sub>2-x</sub> / TCO22-15 1 cm<sup>2</sup> mesoporous CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> PV cells
- Efficiency greater than the sputtered reference
- 14.53%, 13.57% mpp vs 14.11% 13.15% mpp
- Decrease in  $V_{oc}$ , FF,  $J_{sc}$  and hence efficiency with thickness
- Possibility to further improve efficiency with reduced thickness

# Current Density Plots & MMP Tracking



- Increased FF for 40 nm AP PECVD & Sputtered film
- Hysteresis reduced for thinner films – reduced series resistance
- MPP efficiency stable after five minutes

# External Quantum Efficiency

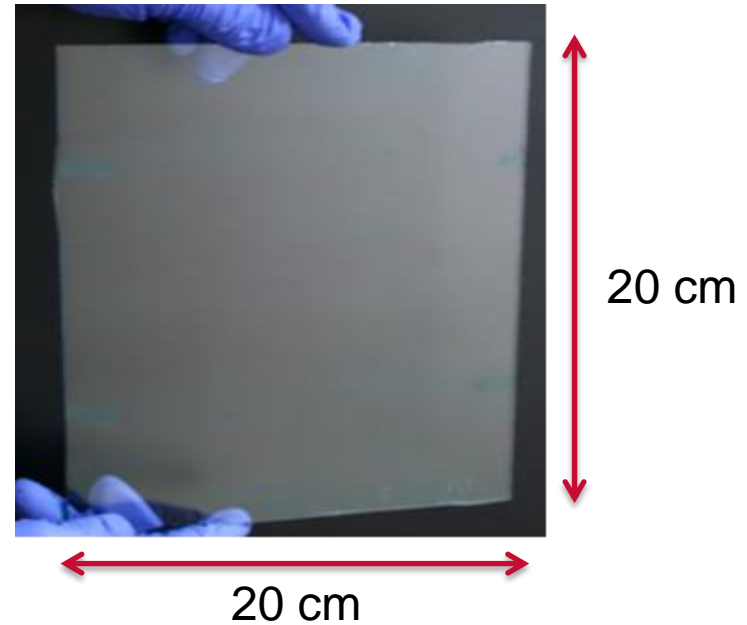
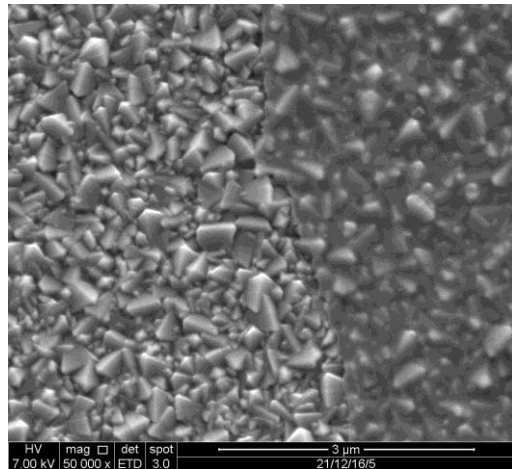
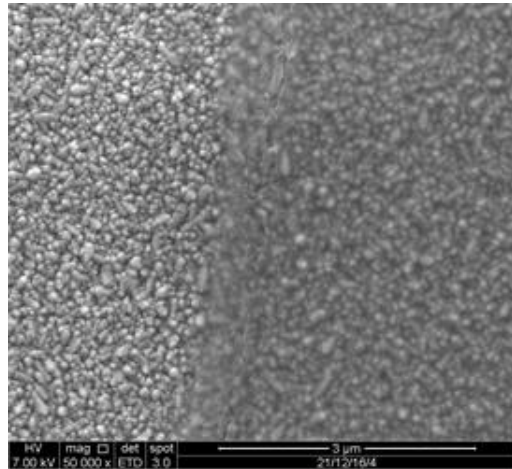


- 40 nm AP PECVD film gave reduced EQE compared to sputtered film
- This deficiency could be completely offset by applying a 0.5 V negative bias
- Collection issue related to an extraction barrier at the interface

## Conclusions and Further work

- $\text{TiO}_{2-x}$  deposited via continuous AP PECVD process
- Film properties and uniformity suitable for ETL
- Excellent cell performance demonstrated by non optimised films
  - 14.53%, 13.57% mpp (AP PECVD) vs 14.11% 13.15% mpp (Sputtered)
- Issues generally related to film thickness ( 40 nm vs 23 nm)
  - Dark conductivity, series resistance, FF
- Significant potential for efficiency gains in conjunction with large area processing
- Further work ongoing to optimise films
  - Repeat characterisation & cell tests with reduced film thickness
  - Compare different substrates – optimal thickness / coverage
  - Explore scale up to 20 x 20 cm
  - Investigate the use of nitrogen plasma

## Further Work



- ~20 nm films deposited on Soloronix TCO 22-15 & NSG TEC 7
- Cell evaluation underway
- Deposition on 20 x 20 cm substrate

# Acknowledgments

Co Authors / collaborators

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