



Rapid optimisation techniques for thin-film materials and devices

Robert Treharne

Functional Thin Films

16th October, Coventry



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News

Viewpoint: The 2014 Nobel Prize in Physics

Ken Durose is Professor of Applied Physics and Director of the University's Stephenson Institute for Renewable Energy .

[Read the full story.](#)

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Outline

- 1) Capabilities
- 2) What I mean by “Combinatorial”
- 3) **Case Study:** Transparent Conductors
- 4) Other Applications
- 5) Other cool stuff





AJA Phase II-J

Multi-source RF sputtering system

ZnO
SnO₂
TiO₂
SiO₂
Al₂O₃

Ta₂O₅
Nb₂O₅
V₂O₅
V₂O₃
ZrO₂

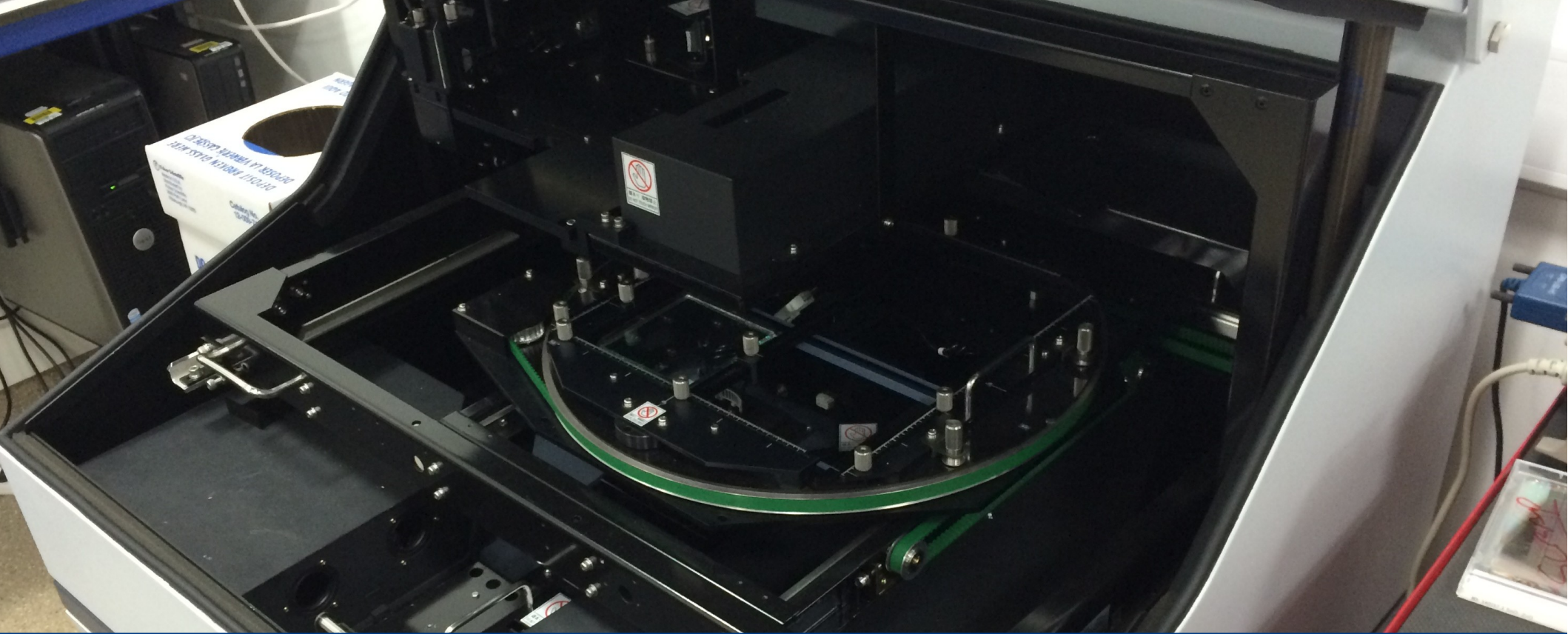
MgO

ZnS
CdTe
ZnTe
CdSe
ZnSe

CdS
Sb₂Te₃
As₂Te₃

Ge
Zn
Nb
Te
Sn

Ag
Ti
Al
Cu
Bi

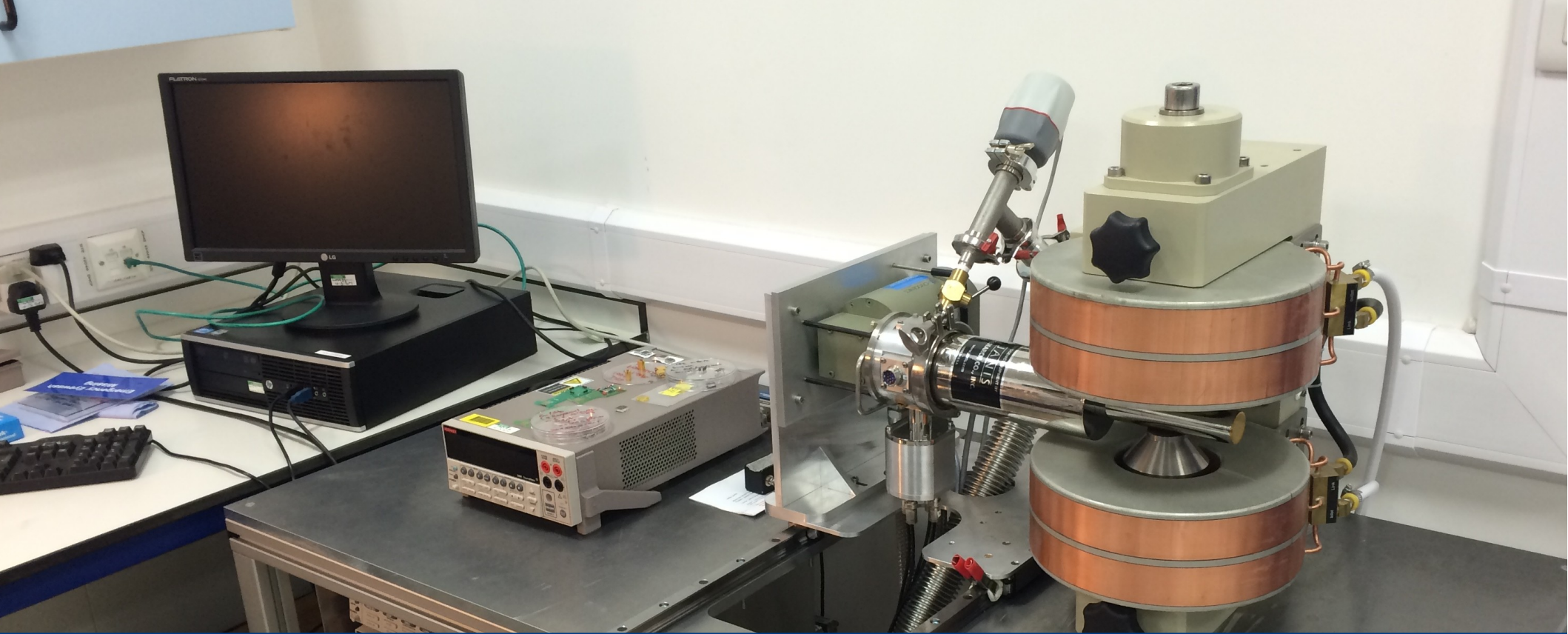


Optical Characterisation

- UV-VIS-IR (250 – 2000 nm): Shimadzu
- Variable Angle Ellipsometry: Woollam
- Both units have **scanning** capabilities



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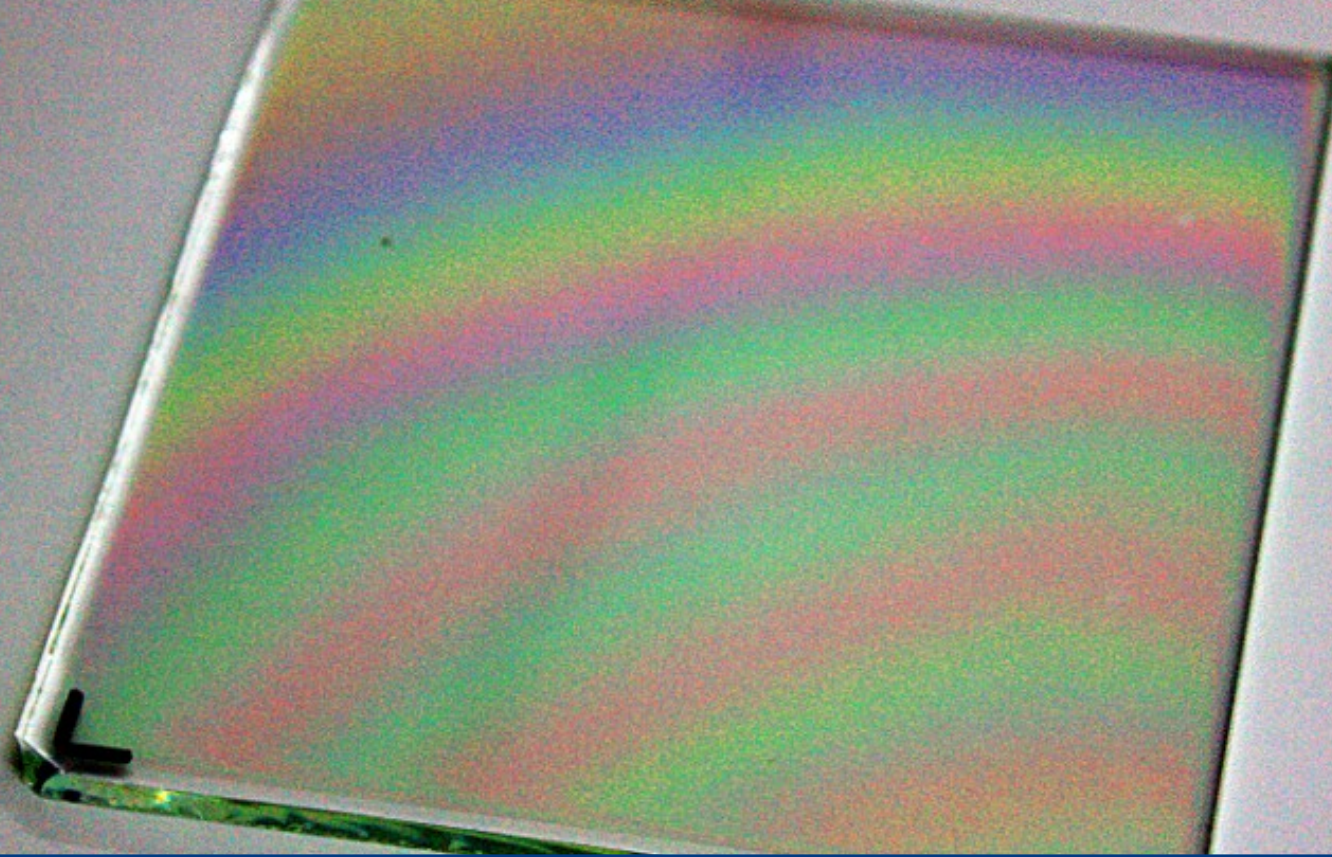


Electrical Characterisation

- Hall Effect – carrier conc & mobility
- 4PP – Sheet resistance – Scanning!



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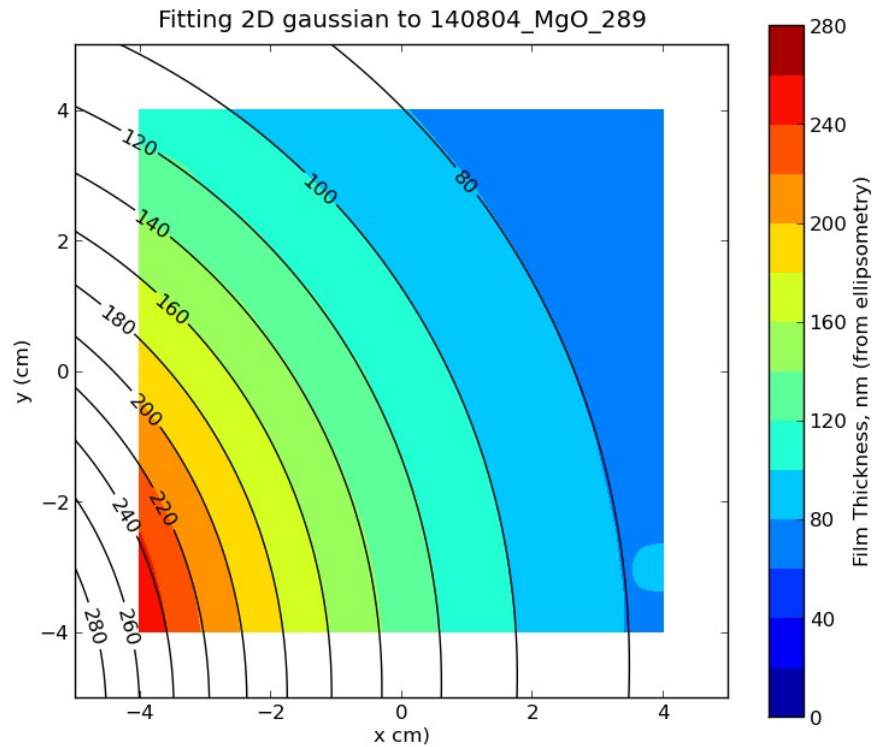


Shhh! Don't say the C-word

“Combinatorial” is sometimes a code term used to describe uncontrolled non-uniform deposition.



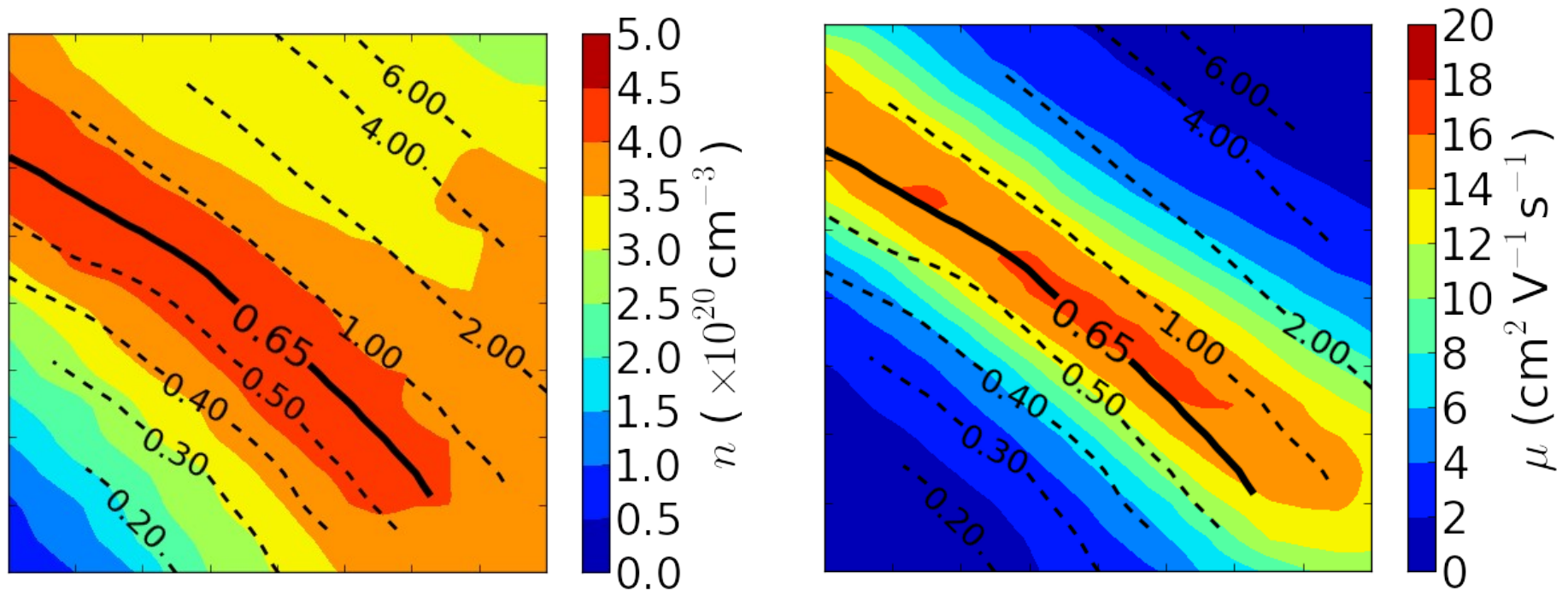
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Controlled Non-Uniformity

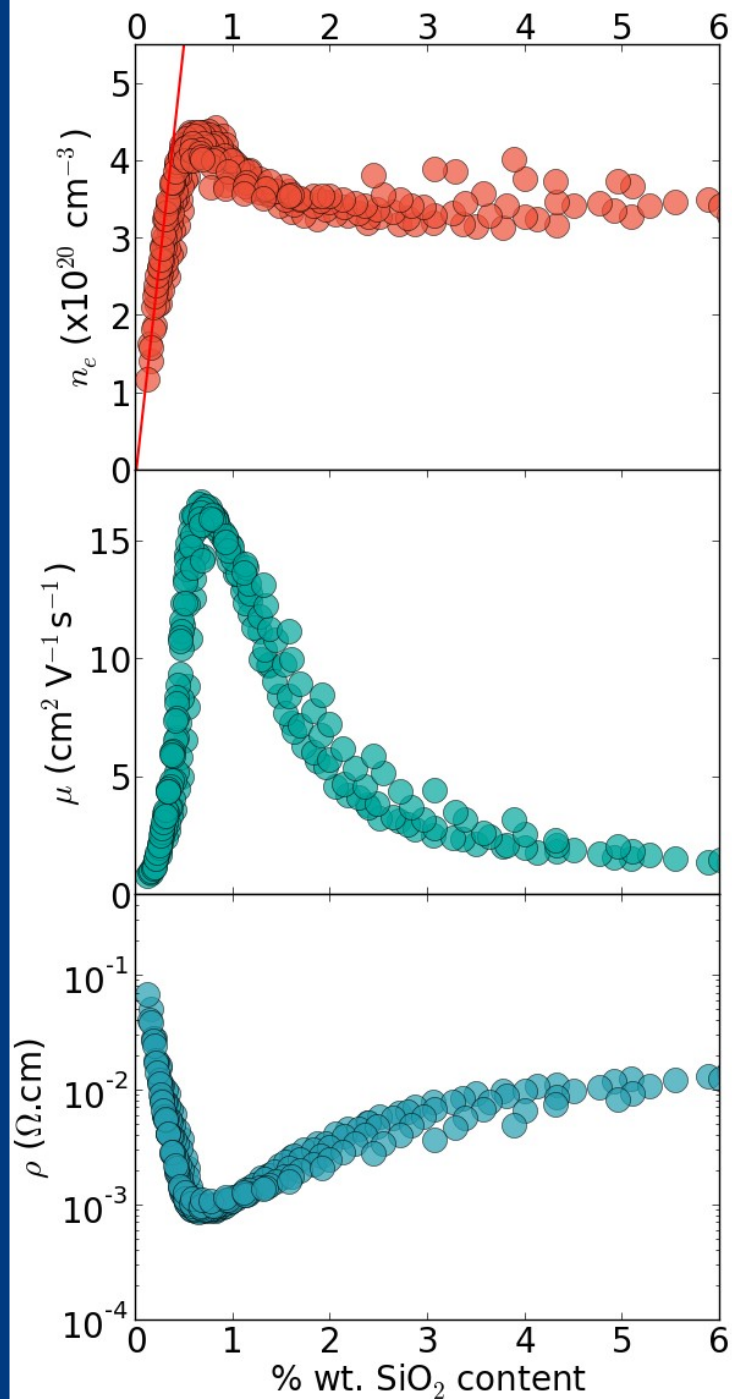
- Profile from each gun described by 2D gaussian
- Excellent control over deposition parameters
- High run-to-run reproducibility
- Can predict multi-gun profiles





Case Study: Transparent Conductors

- Essential materials for PV and consumer electronics
- Combinatorial doping study: Si doped ZnO
- Sample **hundreds** of compositions in a single sample
- Mapping opto-electronic properties vs dopant composition
- Extrapolation!



Can do this in 1 day
(that's a big deal)

Can also extract some
fundamental physics

JOURNAL OF APPLIED PHYSICS 115, 063505 (2014)



Non-parabolicity and band gap re-normalisation in Si doped ZnO

R. E. Treharne,^{1,a)} L. J. Phillips,¹ K. Durose,¹ A. Weerakkody,² I. Z. Mitrovic,² and S. Hall²

¹Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool, United Kingdom

²Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool, United Kingdom

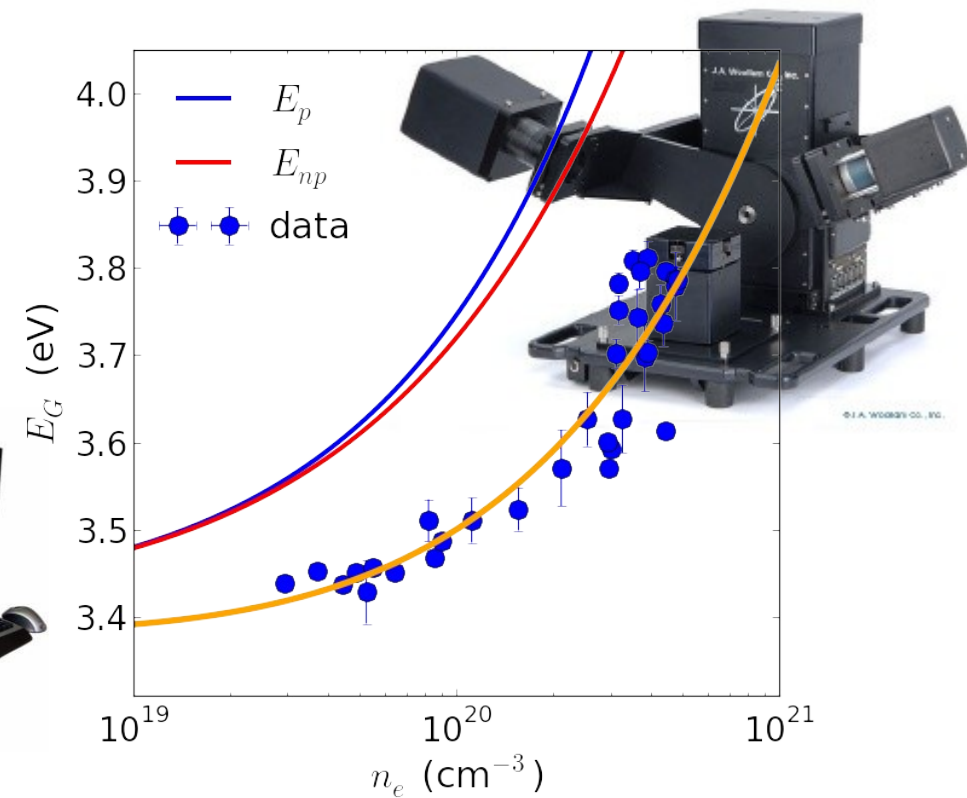
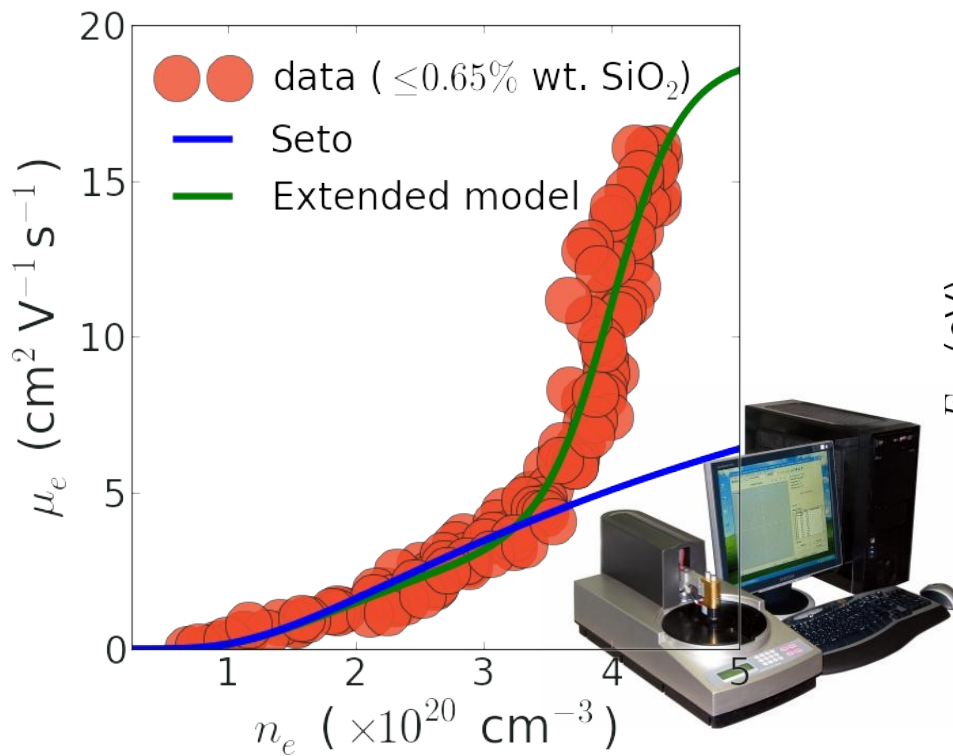
(Received 3 January 2014; accepted 20 January 2014; published online 11 February 2014)

A combinatorial methodology, developed for the rapid optimisation of sputtered transparent conducting oxides, was applied to Si doped ZnO. A wide range of compositions have been explored over a single sample to determine an optimum composition, with respect to the minimisation of resistivity, of $x = 0.65\%$ wt. SiO_2 . A fundamental investigation of the conduction band non-parabolicity yields values of $m_{e0} = 0.35m_0$ and $C = 0.3 \text{ eV}^{-1}$ for the conduction band minimum effective mass and the non-parabolicity factor, respectively. The variation of extracted band gap values with respect to dopant concentration provided an estimate of the magnitude of re-normalization effects. A model is proposed to describe the carrier transport behaviour for a degenerate polycrystalline semiconductor by accounting for the tunnelling of carriers through grain boundaries. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4863875>]

I. INTRODUCTION

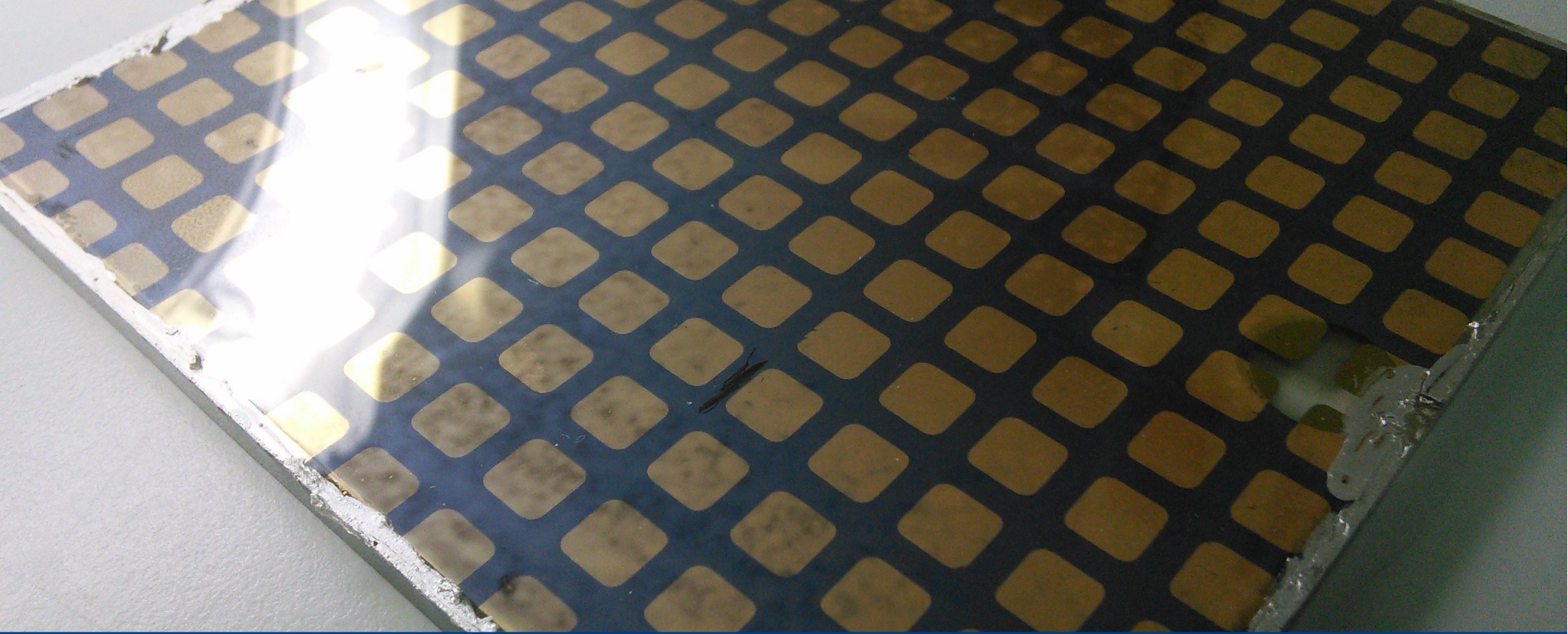
Polycrystalline ZnO films have received significant attention in recent years. They can be degenerately doped, typically by incorporating group III (e.g., Al, Ga, or In (Ref. 1)) or group VII (e.g., F (Refs. 2 and 3) and Cl (Ref. 4)) elements to achieve resistivities of the order of

which there is a spatial variation in either the major element composition or the doping density. Knowledge of the spatial composition variation may then be combined with the results of spatially resolved electrical conductivity measurements (from probes or optical methods) to yield the complete compositional dependence of the electrical prop-



Going deep!

- Effective Mass – dependent on dopant conc.
- Transport mechanisms: Scattering – **new physical models!**
- Electronic structure: Shape of conduction band
- **ALL WITH ONE CONSISTENT SAMPLE!**



Further Applications

Optimising Thin-Film PV

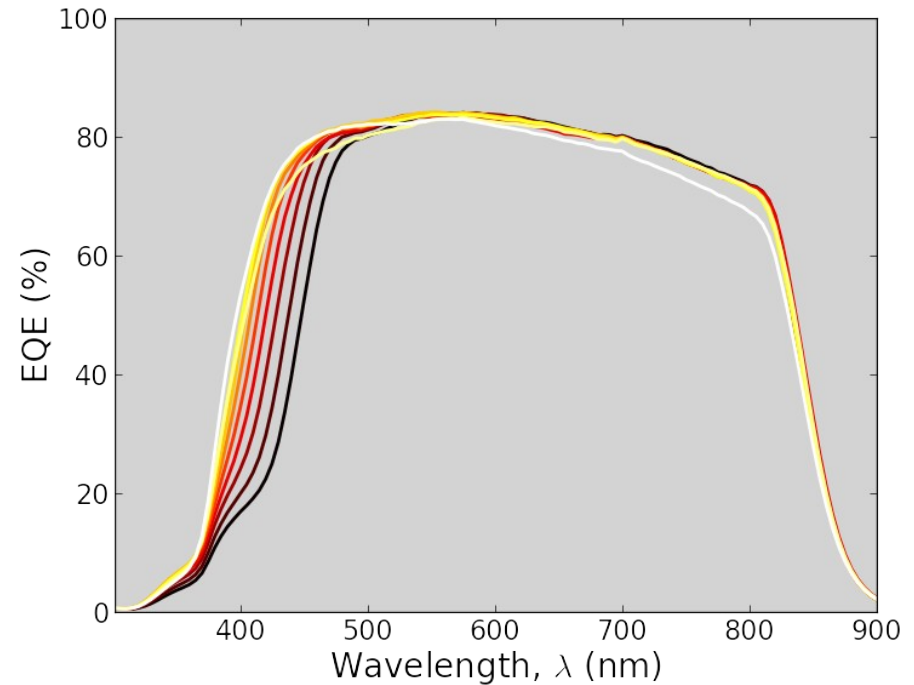
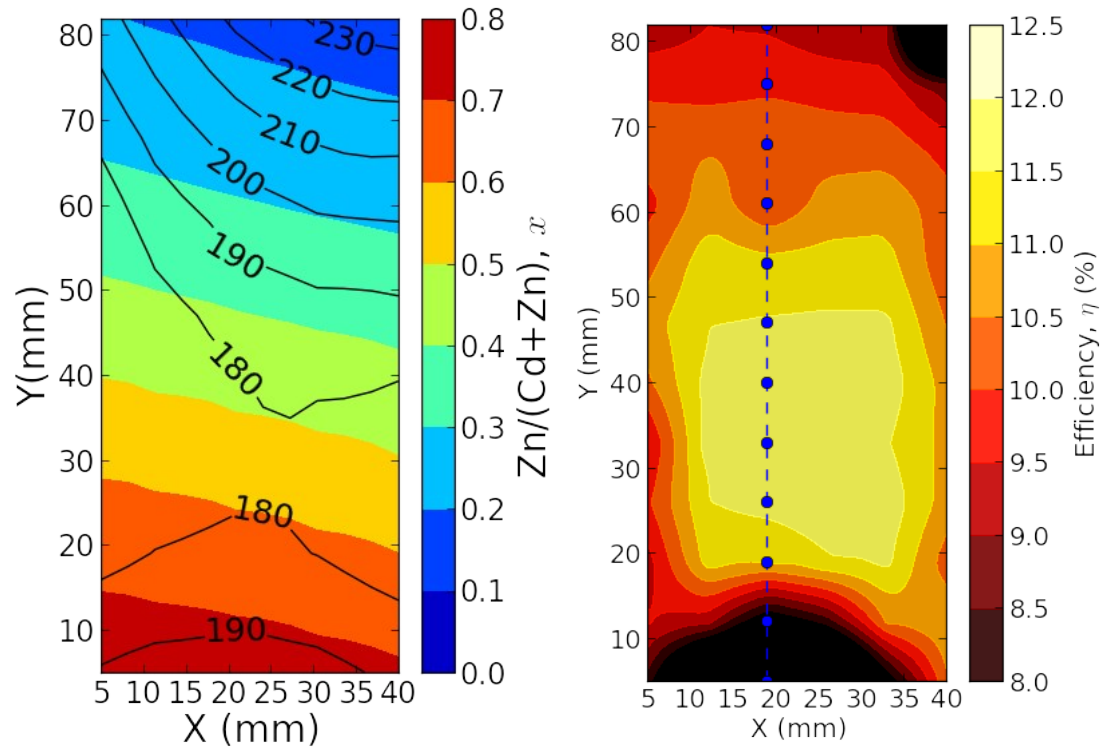
CdTe, CZTS, perovskites

Transparent Electronics

ZnO TFTs



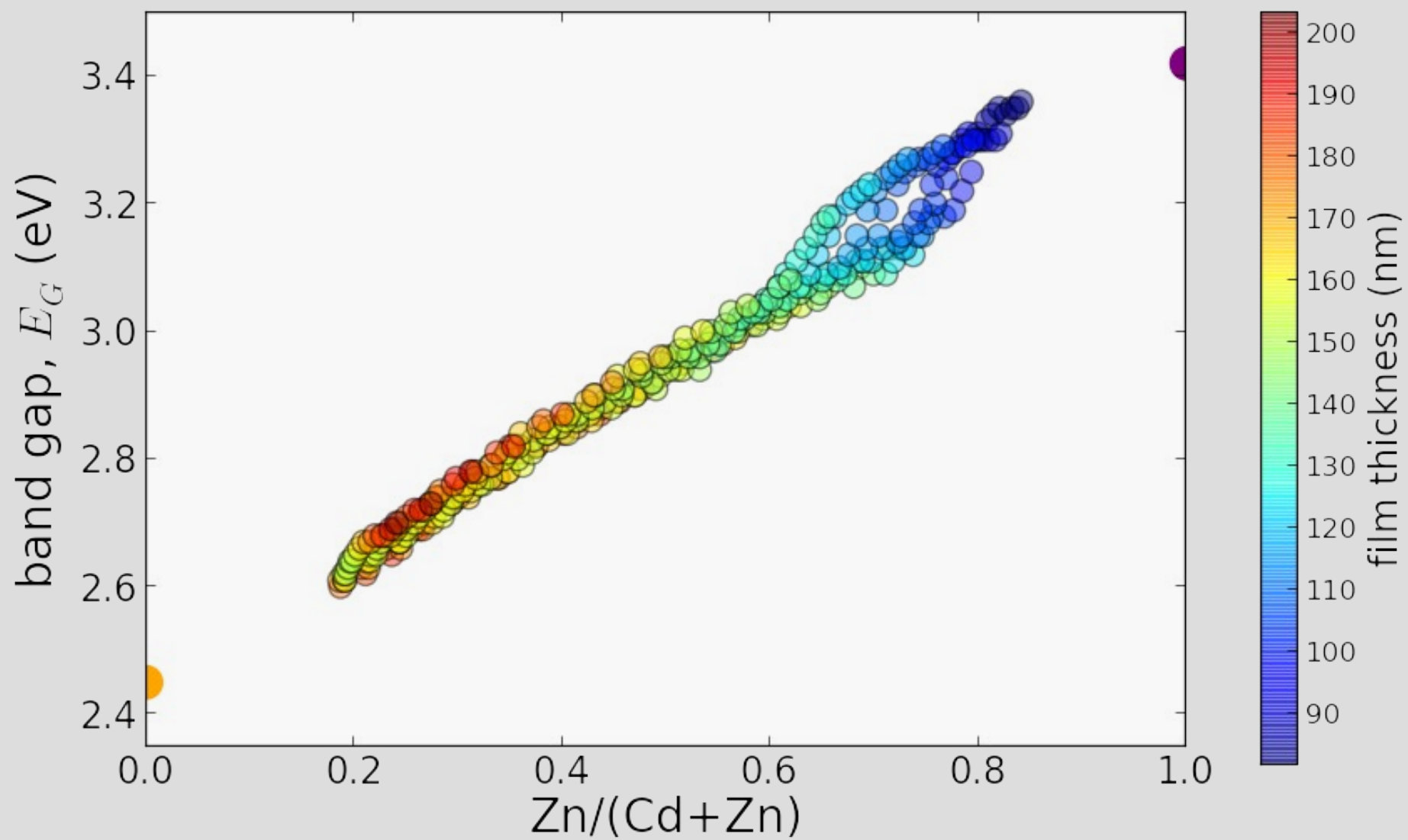
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Example: $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ layers for CdTe TFPV

- Can investigate $x = 0.1 - 0.7$ in one device
- Mapping performance with respect to x
- Optimum $x \sim 0.6$ identified
- Improvement in V_{oc} identified
- Highly consistent data sets





A Combinatorial Approach to the Optimisation of $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ layers for CdTe Solar Cells

Rob Treharne¹, Andy Clayton², Laurie Phillips¹, Jon Major¹, Stuart Irvine², Ken Durose¹

¹Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool, UK

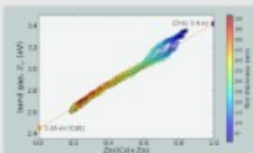
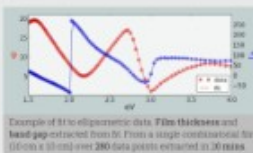
²Centre for Solar Energy Research, University of Glyndŵr, St. Asaph, UK



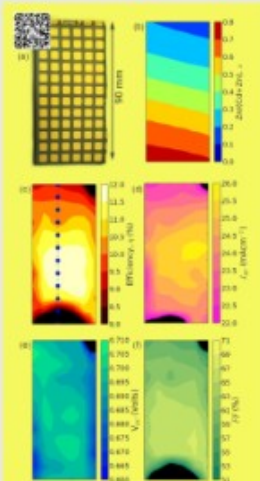
Overview
The optimisation of thin film solar cell performance typically requires a large degree of trial and error and the fabrication of large sample sets. In this work a rapid combinatorial approach to cell optimisation is developed. The method is used to determine the optimum composition of a $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ window layer that maximises the performance of a CdTe based device structure. A large consistent data set (over 70 cells) was generated from the fabrication of a single sample.



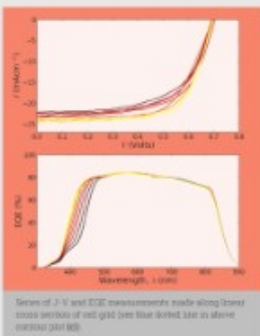
Measurement and analysis of a combinatorial $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ film was fully automated using scanning ellipsometry. A $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ film was incorporated into a CdTe based device structure as an n-type window layer and an automated J-V measurement system was used to map the performance over a grid of 72 cells.



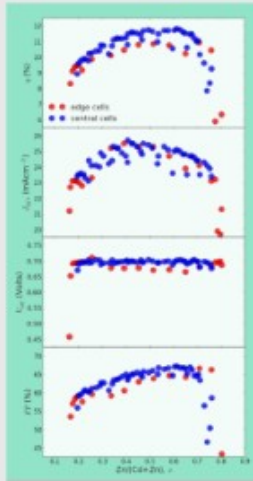
Relationship between band gap and composition of $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ film extracted from automated ellipsometry. The data set (289 points) is highly consistent but shows some scatter for ZnS thicknesses below 100 nm.



(a) Composite CdTe device with grid of 72 cells. (b) Map of $\text{Cd}/(\text{Cd}+\text{Zn})$ window layer composition in device. (c) (f) Maps of conversion efficiency and relevant performance parameters.

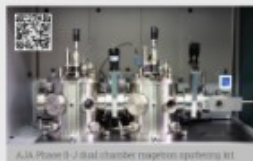


Series of J-V and EQE measurements made along linear cross sections of cell grid (see blue dotted line in above micrograph for cell).



Measured device parameters plotted with respect to x . Cell efficiency increases with increasing x up to a value of $x = 0.57$. Beyond this the efficiency drops off rapidly. The variation in efficiency is dominated by changes to the FF factor.

An unambiguous relationship has been determined between composition of the $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ window layer and cell efficiency. An optimum value of $x = 0.57$ was identified. J-V measurements show that gains in the series resistance. EQE measurements show that further increases in J_{sc} are limited by the band gap of the HRT ZnO layer (~ 3.2 eV). The combinatorial approach generates large and highly consistent data sets from a single sample. This permits the rate at which investigations can be made to be greatly increased.



AJA Power 3-J dual chamber magnetron sputtering kit

A Combinatorial Approach to the Optimisation of $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ Layers for CdTe Solar Cells

Robert E. Treharne¹, Andrew Clayton², Laurie J. Phillips¹, Jonathan D. Major¹, Stuart J. C. Irvine², Ken Durose¹

¹Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool, L69 7ZF, Merseyside, UK

²Centre for Solar Energy Research, University of Glyndŵr, St. Asaph, LL17 0JD, Denbighshire, UK

Abstract—A combinatorial methodology has been adopted to determine the optimum composition of a $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ window layer for CdTe solar cells. The methodology generated a large, self consistent dataset which permitted an unambiguous relationship between x , conversion efficiency and related cell parameters to be determined. An optimum composition of $x = 0.57$ was shown to maximise cell efficiency. Analysis of $J-V$ curves, measured over 72 separate cells show that both short circuit current, J_{sc} , and fill factor, FF , values increase with respect to x over the

II. EXPERIMENTAL

A. Deposition and Characterisation of $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ Films

Deposition of $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ films was achieved by co-sputtering from separate CdS and ZnS targets (3" dia. Pi-Kem Ltd, UK) using RF powers of 100 W and 200 W respectively and an Ar pressure of 5 mTorr. The composition profile was achieved by switching off the substrate

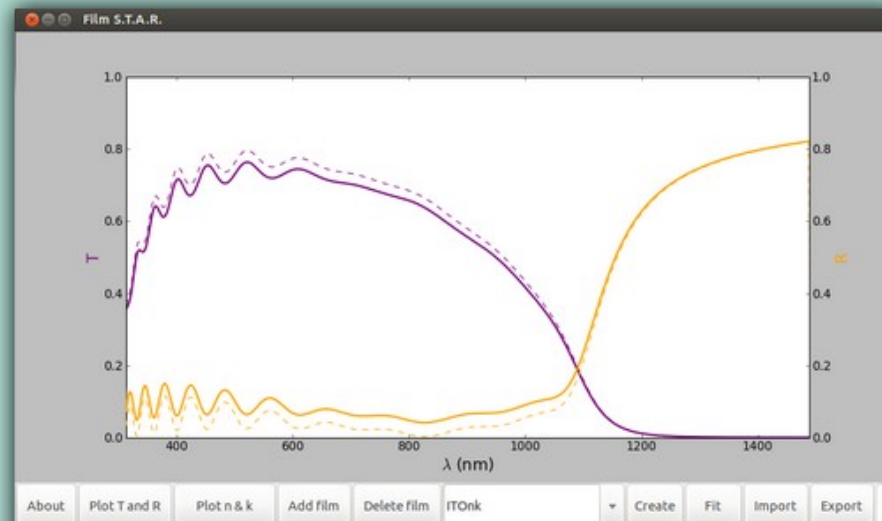
Recently presented at
40th IEEE PVSC Colorado

Film S.T.A.R (Simulated Transmission and Reflection)

Optical modelling of multi-layer structures: A user-interface to the transfer matrix method.
Version 2.5



Screenshot



Other Stuff

Film S.T.A.R

Thin-film optical database

Multi-layer modelling

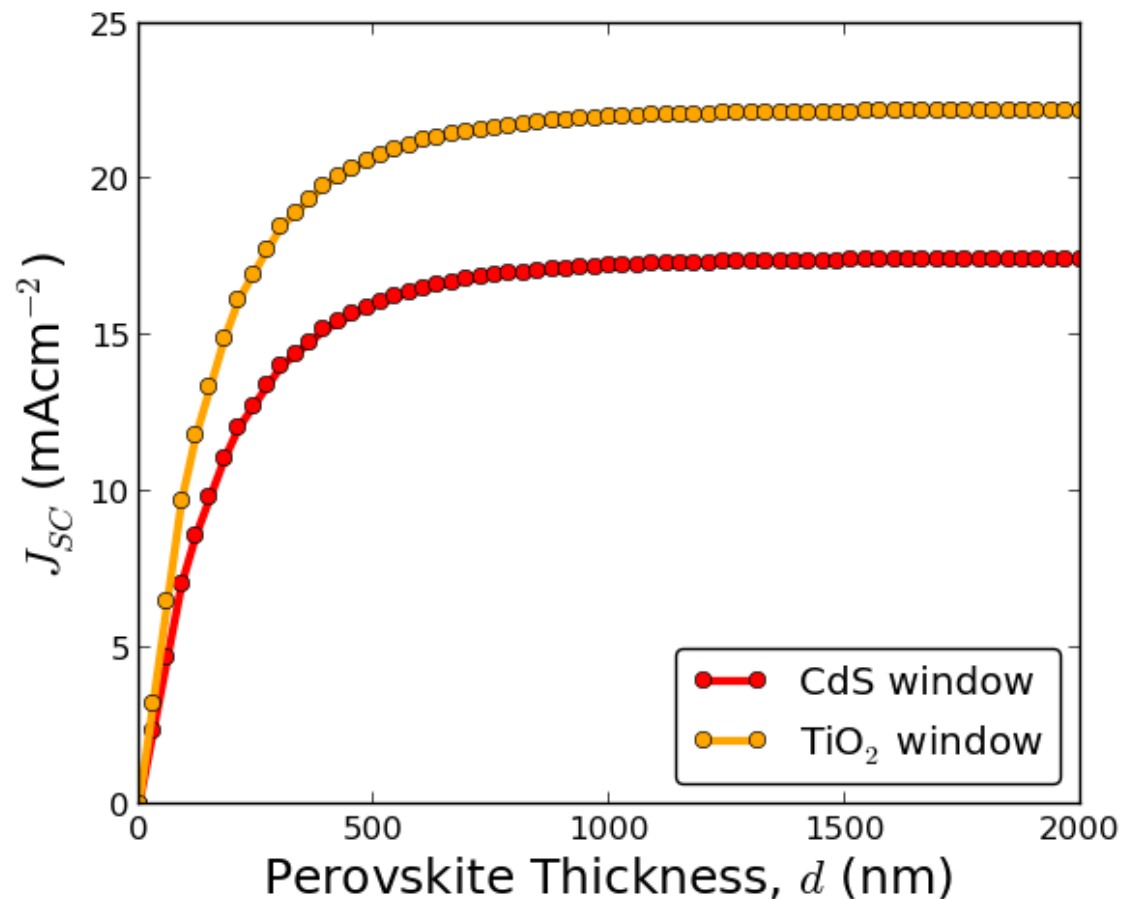
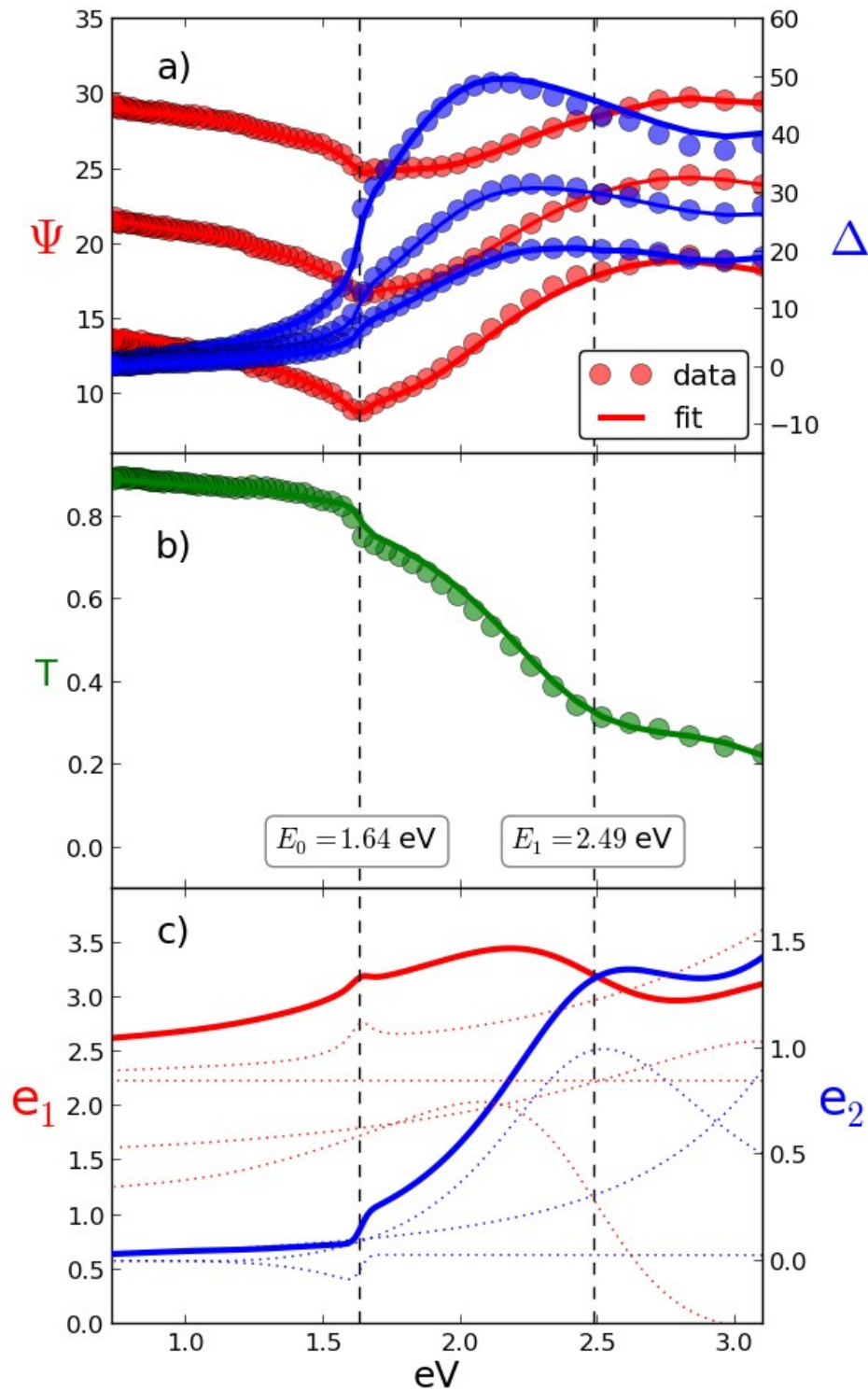
Currently developing public webapp



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Perovskite!

- Ellipsometry of perovskite film
- n and k extracted
- Multi-layer model to determine optimum thickness for device





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News > Science

Breakthrough in solar panel manufacture promises cheap energy within a decade



LETTER

doi:10.1038/nature13435

A low-cost non-toxic post-growth activation step for CdTe solar cells

J. D. Major¹, R. E. Treharne¹, L. J. Phillips¹ & K. Durose¹

...ly established as the basis for cell technology. With laboratory the research and development of power generation further (ref. 2) and to minimize the of the manufacturing process in-film CdTe with CdCl₂. This on at the CdTe/CdS interface^{3,4}, making it essential in achiev- although such doping has been ment of this processing route vere disadvantages; it is both and a water-soluble source of risk to both operators and th ere we demonstrate that solar non-toxic and costs less than a nd 13%) identical to those o have similar hole density comparable impurity prof

Cl and O, these elements being important p-type dopants for CdTe thin films. Contrary to expectation, CdCl₂-processed and MgCl₂-processed solar cells contain similar concentrations of Mg; this is because of Mg out-diffusion from the soda-lime glass substrates and is not disadvantageous to device performance. However, treatment with other low-cost chlorides such as NaCl, KCl and MnCl₂ leads to the introduction of electrically active impurities that do compromise device performance. Our results demonstrate that CdCl₂ may simply be replaced directly with MgCl₂ in the existing fabrication process, thus both minimizing the environmental risk and reducing the cost of CdTe solar-cell production.

The cost of CdTe photovoltaic modules has now dropped below one US dollar m⁻² and the power generation is rapidly approaching that of silicon. The fabrication of CdTe solar cells in the presence of CdCl₂ results in a cell with <2% efficiency and is linked to the use of toxic CdCl₂ in both the growth and post-growth steps. The



THE **NAKED** SCIENTISTS

Other Stuff

Recent breakthroughs

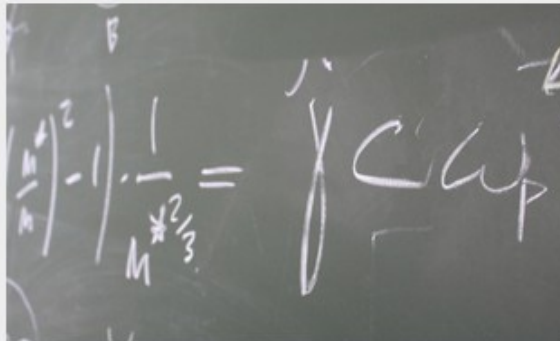
MgCl₂ activation of CdTe solar cells

No need for toxic CdCl₂

CdTe: Old dog, new tricks!



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Fundamentals for New and Sustainable
PV

Liverpool
Nov 3rd - 14th



Renewable Energy, Developing World,
Entrepreneurship

Cambridge
Dec 1st - 12th



Research Skills and PV in Action

Sheffield
Jan 12th - 23rd

EPSRC CDT in Photovoltaics

Starts in November!

£8m investment

7 University partners

65 PhD students

Publically available resources



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Rapid optimisation techniques for thin-film materials and devices

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