CMRI

Band engineering of TiO_2 for efficient low-cost solar cells

University of Bolton

Professor Guosheng SHAO

Centre for Materials Research & Innovation (CMRI)
University of Bolton

CMRI

Current problems of Si solar cells

University of Bolton

High cost and long pay back period:

- For an average UK home, 4 years for energy payback, 20 years for financial return
- The life time 25 years → little financial benefit left

No other PV as competitor, annual market growth ~ 40% !!!

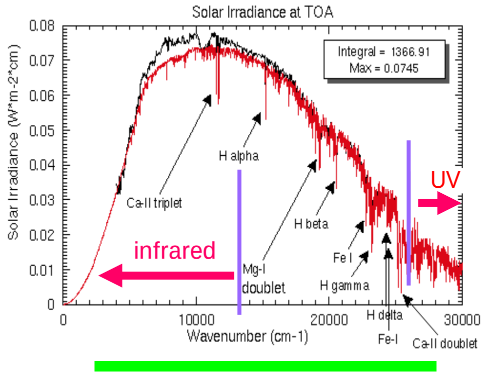
Worrying Si price: $25/kg (2004) → $300/kg (2007)

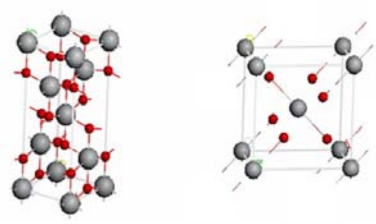
Government's target for 5% solar energy for domestic use by 2015 possible ???

PV is hot for wealth creation while GREEN (China 2001 on 50% annual growth – now 3rd largest PV manufacturer), driven by low-cost labour

PV is key for solar water splitting

Significantly narrowed TiO_2 band gap desired





Anatase
3.2 eV

Rutile
3.0 eV

UV 5% only !!!

➢ ***Feasible to achieve significant redshift by alloying ???***

Current status of dye-sensitised TiO_2 solar cells (Graetzel et al, Nature 1991)

Attractive low cost for production (~1/4 of thin film Si SC); no pn junction.

But:

Low efficiency with energy heavily wasted at:

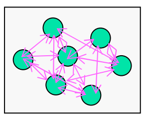
- dye-TiO_2 interface (large angle phase boundaries)
- waste due to intraband transitions

Short life due to oxidation of organic dyes

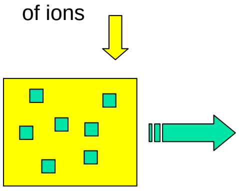
OBJECTIVES: DFT modelling for *effective alloying schemes*

- *Elements of significant effect on narrowing band gap*
- *Thermodynamic feasibility for alloying*

Density functional method (DFT)



Interacting electrons & field of ions



Fictitious **non-interacting** electrons & V_{eff} [n]

$$E[n] = T[n] + \underbrace{V_{ee}[n] + V_{xc}[n] + V_{ext}[n]}_{\int v_{eff}(\vec{r})\, n(\vec{r})\, d\vec{r}} + E_{pp}$$

$$V_{ee} = e^2 \int \frac{n(\vec{r})\, n(\vec{r}\,')}{|\vec{r}\,' - \vec{r}\,|}\, d\vec{r}\, d\vec{r}\,' \qquad \text{Hartree potential e} - \text{e}$$

$$V_{ext} = \int V(\vec{r})\, n(\vec{r})\, d\vec{r} \qquad \text{electron} - \text{core } \textit{potential}$$

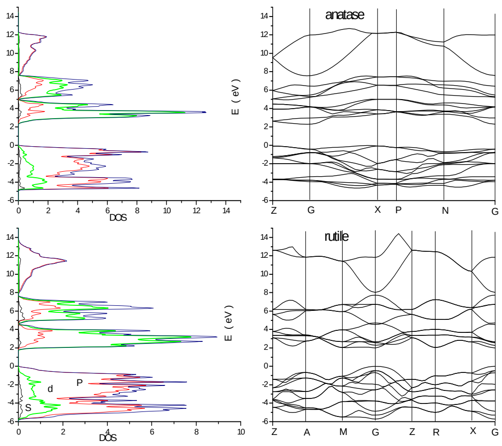
$$V_{xc} = \underbrace{\int n(\vec{r})\, \varepsilon_{xc}[n(\vec{r})]\, d\vec{r}}_{\text{LDA}} \qquad \text{exchange} - \text{correlation potential}$$

$$\delta E[n] = 0, \text{ with the limiting condition } \int n(\vec{r})\, d\vec{r} = N$$

$$\Rightarrow E[n] \rightarrow E_0[n]$$

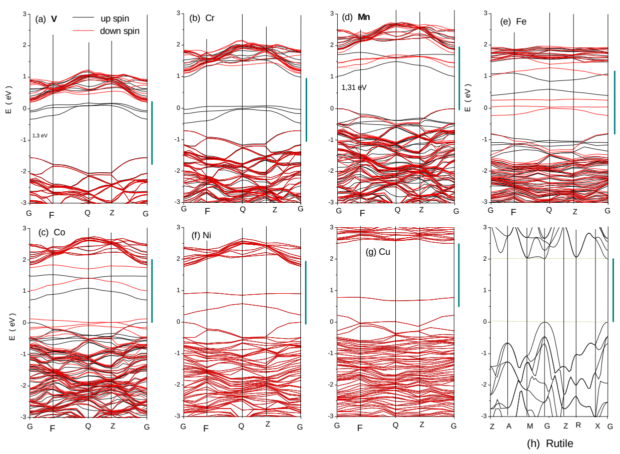
$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{eff}(\vec{r}) \right\} \phi_i(\vec{r}) = \varepsilon_i\, \phi_i(\vec{r}) \qquad \text{Kohn} - \text{Sham equations}$$

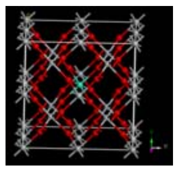
Pure TiO_2 phases



- Anatase indirect gap
- Rutile direct gap
- Rutile 0,2 eV narrower
- Useful for low-cost and long-life PV, should band gap be effectively narrowed.

2x2x2 SC + 3d metal subs.





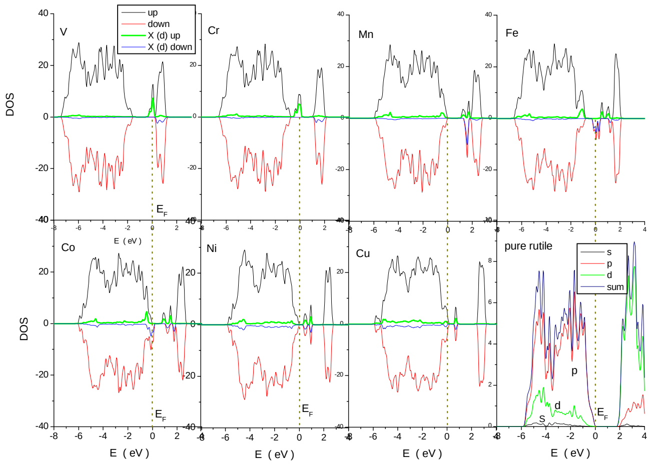
2x2x2 SC

- interband
- narrowed gap
- X(d)-p IB levels more localised when d-shell --> complete

CMRI

University of Bolton

Typical DOS



- IB due to X(d) and O p hybridisation.
- spin-polarisation associated with in-complete d-shells.

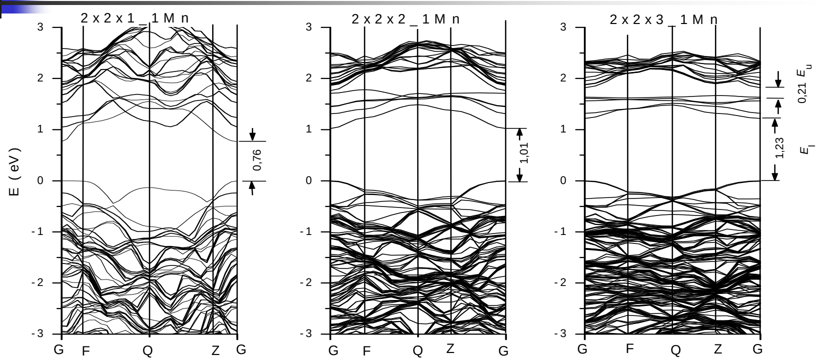
www.bolton.ac.uk

Guosheng Shao

CMRI

University of Bolton

Compositional dependence: Mn example



1/8 subs. 1/16 1/24

- ***Mn replacement of Ti sites are effective in narrowing the bandgap***
- ***6,25 % Mn substitution of Ti sites causes over 50 % gap narrowing***
- ***Direct gap***

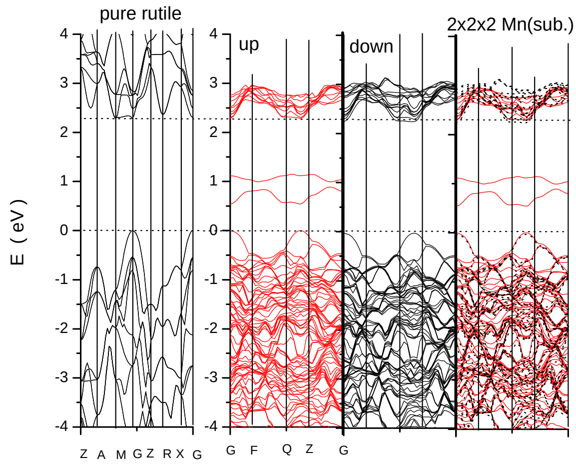
www.bolton.ac.uk

Guosheng Shao

CMRI

University of Bolton

Refined model: DFT+U



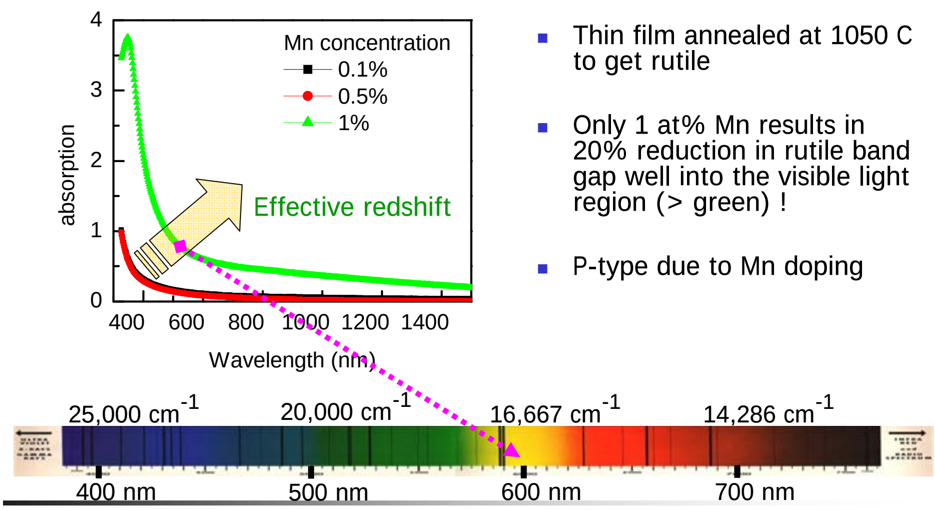
- U to host Ti to open gap;
- U to doping atom to lower IB;
- Effective only to spin-polarised IB states

www.bolton.ac.uk Guosheng Shao

CMRI

University of Bolton

Experimental verification



- Thin film annealed at 1050 C to get rutile
- Only 1 at% Mn results in 20% reduction in rutile band gap well into the visible light region (> green) !
- P-type due to Mn doping

www.bolton.ac.uk Guosheng Shao

CMRI

University of Bolton

Funding & staff

- Joule Funding £35,071 for 1 yr
- Partial financing PhD students together with UoB studentship:

  Kenan Song; Larry Lan;

  Shiva Boppona

www.bolton.ac.uk Guosheng Shao

CMRI

University of Bolton

Deliverables

- 1 patent application on novel solar cells
- TSB project on novel solar cells ***£910,000***
- Formation of spin-off, with Energi Holdings investment of ***£120,000***
- 3 journal papers: (1 in press of J. Phys. Chem.; 2 papers under prep)
- 1 conf paper published in CMRS 2008

www.bolton.ac.uk Guosheng Shao

CMRI

University of Bolton

acknowledgement

- Joule Centre for exceptional support
- Prof Y Gao, Hubei U, China, for thin film fabrication
- NW Envirolink for introducing industrial links