GCEP Distinguished Lecture
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Third Generation Photovoltaics

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Photovoltaics Centre of Excellence
supported by the Australian Research Council,
the Global Climate and Energy Project
and Toyota CRDL
School of Photovoltaics & RE Eng.

ARC Photovoltaics Centre of Excellence

Stuart Wenham, Martin Green + Management Committee

PV and Renewable Energy
U/G degrees

Laboratory Development

1st Generation:
Wafers

2nd Generation:
Thin Films

3rd Generation: PV
High eff and thin film

Silicon Photonics
Si light emission
School of Photovoltaics & RE Eng.

History

• PV research, UNSW Electrical Eng. 1974 – 1998
• Buried contact solar cell
  – Martin Green, Stuart Wenham 1986
• Crystalline Si on glass spin off company 1995
• Separate Centre 1999 – 2005
• First UG program - Photovoltaics 2000
• PG coursework program 2001
• Second UG program – Renewable Energy 2003
• New School formally declared 2006
UNSW International Collaborations

• DARPA & U. Delaware (50% efficient solar cell)
• Global Climate & Energy Project, Stanford (1)
• Global Climate & Energy Project, Stanford (2)
• Toyota Central R&D Labs.
• Suntech, Wuxi (NYSE)
• Nanjing PV Tech, Nanjing (NASDAQ)
• JA Solar, Ningjin (NASDAQ)
• E-Ton Solar, Taiwan
• Asia-Pacific Partnership (Australia, China, India, Japan, Korea, India, USA)
UNSW Photovoltaics R&D Commercialisation

• First Generation Photovoltaics
  – Buried contact cell (UNSW, BP Solar)
  – Inkjet printing (UNSW, Suntech, E-Ton)
  – Semiconductor Fingers (UNSW, Suntech, E-Ton)
  – Laser doping (UNSW, Suntech)

• Second Generation Photovoltaics
  – Crystalline Silicon on Glass (UNSW, CSG Solar)

• Characterisation Equipment
  – Photoluminescence characterisation (UNSW, BT Imaging)
Undergraduate Education

Two 4-year Engineering programs (189 students):
• Photovoltaics and Solar Energy (2000) (101 students)
• Renewable Energy (2003) (88 students)
Postgraduate Education

- **Master of Engineering Science in Photovoltaics and Solar Energy** (14 students)
  - 1.5 year addition to UG;
  - PV devices; PV systems;
    RE technologies;
- **Research degrees**
  - PhD (47 students)
  - MPhil (10 students)
UNSW Centre for Energy and Environmental Markets

- Interdisciplinary research in energy and environmental markets, policy
- Faculties of Engineering and Commerce & Economics
- Environmental sustainability:
  - eg. PV load & pricing at Olympic Village
- Economic tools & climate change:
  - e.g. Market design (Aust. Stock Exchange, CSIRO)
- Sustainable technology:
  - e.g. Stochastic renewable energy (wind).
- Aust. Greenhouse Office
Third Generation Photovoltaics

Outline

• The importance of Photovoltaics
• Three generations of Photovoltaics
• The main losses in photovoltaic cells
• Third Generation approaches
  • Silicon nanostructure tandem cells
    • Band gap engineering – quantum confinement
    • Fabrication of materials / devices
  • Hot Carrier cells
    • Contacts – energy filtering
    • Hot Carrier cooling – energy loss to phonons
  • Modification of the solar spectrum
    • Up- and Down-conversion
• Potentialities and Viabilities
• Summary
Transforming the global energy mix:
The exemplary path until 2050/2100
appointed for a term of four years by the federal cabinet (Bundeskabinett)

Meeting the IPCC target of 60% reduction in GHG emission by 2050
Booming Photovoltaics

Market growth at 35%/yr for last 10 years, 60%+ in 2007
Approx 1 million jobs in PV by 2020
Approx 1 million jobs in RE by 2010

Global PV market
US$6.5 billion in 2006
→ $16.4 billion in 2012

Driven by rebates/tariffs:
Japan, Germany
Now other Euro. Countries and S Australia

USA: Power purchase agreements

Japan: market is stable with reducing rebates
Learning curves

- more potential for learning
- lower cost at smaller volumes
Photovoltaics: Three Generations

- III-V tandem
- mc-Si
- a-Si tandem
- c-Si

Cost, US$/m²

Efficiency, %
Efficiency Loss Mechanisms

1. Sub bandgap losses
2. Lattice thermalisation

Two major losses – 50%

Also: 3. Junction loss
4. Contact loss
5. Recombination

Limiting efficiencies
- 1 sun
- Single p-n junction: 31%
- Multiple threshold: 68.2%
Third generation options

- Circulators
- Tandem (n\to\infty)
- Hot carrier
- Thermal, thermoPV, thermionics
- Tandem (n = 6)
- Impurity PV & band, up-converters
- Impact ionisation
- Tandem (n = 3)
- Down-converters
- Single cell

One photon
Multiple electrons

\begin{align*}
E_g &\rightarrow E_h \\
E_f &\rightarrow E_{\text{rel}} \\
E_{\text{lev}} &\rightarrow E_i \\
J_l &\rightarrow J_h \\
J_{\text{rel}} &\rightarrow J_{\text{lev}}
\end{align*}
Silicon based Tandem Cell

Martin Green, Gavin Conibeer, Dirk König, Eunchel Cho, Tom Puzzer, Yidan Huang, Shujuan Huang, Dengyuan Song, Angus Gentle, Ivan Perez-Wufl, Chris Flynn, Jeana Hao, Sangwook Park, Yong So, Bo Zhang

Free choice or Si cell

Decreasing band gap

Sunlight

AM1.5G Efficiency

Number of cells

Intrinsic radiative and Auger losses included
Silicon based Tandem Cell

Decreasing band gap:

- Solar Cell 1
- Solar Cell 2
- Solar Cell 3

Anneal 1100°C
- Si precipitation

2nm QD, $E_g = 1.7\text{eV}$

Thin film Si cell
- $E_g = 1.1\text{eV}$

Engineer wider band gap Si QDs

Zacharias, 2000
Si QD characterisation

**XRD Si QDs in oxide** $d_{QD}$ 4.5nm

**PL optical energy levels**

**Diameter of Si QDs [nm]**

$\begin{array}{c|c|c|c|c}
\text{Deposition time [sec]} & 100 & 150 & 200 & 250 \\
\hline
\text{Integrated PL intensity [au]} & 30000 & 25000 & 20000 & 15000 \\
\text{Integrated PL energy [eV]} & 5000 & 10000 & 15000 & 20000 \\
\end{array}$
Range of QD materials

Alternative matrices

Greater $\sigma$ for Si$_3$N$_4$ but also lower $E_{\text{act}}$

DFT modeling
Various material combinations

Quantum Dot / Matrix combinations and current status of investigations

<table>
<thead>
<tr>
<th>Decreasing processing temperature</th>
<th>Increasing conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>SiO₂</td>
</tr>
<tr>
<td>SPOED</td>
<td>SPOED</td>
</tr>
<tr>
<td>Ge</td>
<td>SP</td>
</tr>
<tr>
<td>Sn</td>
<td>SPO</td>
</tr>
</tbody>
</table>

S = Simulation (ab-initio modelling - DFT)
P = Physical (electron microscopy, X-ray diffraction)
O = Optical (photoluminescence, absorptance)
E = Electronic (conductivity, conductivity with Temp.)
D = Devices (Diodes, Cells)
Hot Carrier solar cell

Started September 2008

University of New South Wales, Sydney:
Gavin Conibeer, Martin Green, Dirk König, Shujuan Huang, Santosh Shrestha, Chris Flynn, Lara Treiber, Pasquale Aliberti, Andy Hsieh, Rob Patterson, Binesh Puthen Veettil, Martin Kirkengen

Institute Energie Solar, Universitas Polytechnic Madrid:
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Inst. Research Development Energie Photovoltaic / CNRS, Paris:
Jean Francois Guillemoles, Lunmei Huang

University of Sydney:
Timothy Schmidt, Raphael Clady, Murad Tayebjee
Hot Carrier cell

Extract hot carriers before they can thermalise:

- Need to slow carrier cooling
- Collect carriers over narrow range of energies
- Renormalisation of electron (hole) energies

\[ \Delta \mu_A = qV \]

Würfel, SOLMAT, 46 (1997) 43 1995
Green, 3rd Gen PV (S-Verlag) 2003
Würfel, PIP, 13 (2005) 277
Conibeer, TSF, 516(2008) 6948
Takeda et al, SOLMAT, 08
Resonant Tunneling Transport

Energy Selective Contact

Filter

NDR at 300K - Repeatable

Gate voltage (V)

0 0.5 1 1.5

log(A)

0 0.01 0.02 0.03 0.04

Two different sites on the wafer

Dielectric matrix

Si QD

Resonant Transport

I

V
Hot Carrier cooling

Electrons carry most energy

Cool predominantly via small wave vector optical phonon emission - timescale of ps inelastic – energy relaxation

Hot Optical phonon population “phonon bottleneck effect”

Decay of Optical phonons to Acoustic is critical

Slows further carrier cooling
Optical phonon decay
Optical phonon decay

$O \rightarrow \text{LA} + \text{LA}$ (Anharmonicity or Klemens mechanism)
Allowed phonon energies

Element – e.g. Si

Compound – e.g. InN

Optical phonons (standing waves)

Acoustic phonons (heat in the lattice)

Some evidence for slowed carrier cooling in InN: Chen & Cartwright, APL, 83 (2003) 4984

And for longer phonon lifetimes in GaN, AlSb, InP – all of which have large phonon gaps
Phononic band-gaps for various binary compounds

$E_{g} = 0.7\text{eV}$
Phononic gaps in nanostructures

Linear force constant model: \( l = 4a_1 + 4a_2 \)
- mass ratio = 2; force constant ratio = 5
Phonon propagation in nanostructure

Acoustic phonon reflected from zone edges → standing wave
1D to 3D modelling

Uniform 3D periodic QD array

- Coherent interference
- Periodic QD array – probably fcc – probably core shell QDs
- 1D modelling to 3D – Lunmei Huang
- Long range / short range defects – Andy Hsieh, Binesh PV
Colloidal dispersion of nanoparticles

• Colloidal dispersion of Si or other nanocrystals – want uniform spacing and mono-disperse size

• Core shell nanocrystals – hetero-interface – Guillemoles, IRDEP, Paris

Langmuir-Blodgett deposition of monolayers build up multiple mono-layers

Organosilanes of varying alkyl chain lengths –
  a) Trimethoxy(propyl)silane, b) Trimethoxy(octyl)silane
Towards a complete cell

- Fabrication of slowed cooling absorber
- Transport and Renormalisation of carrier energies
- Energy Selective Contacts
Modification of the incident solar spectrum

Down conversion

PV cell

One photon

Multiple electrons

Multiple exciton generation (MEG)
Hanna, Nozik, JAP (2006) 100, 074510
Schaller, Klimov, PRL (2004) 92, 186601

either: Inject two e-h pairs into cell
or: Re-emit two photons above $E_g$ of cell

QE > 100% to be useful
i.e at least as many photons out as in

PbSe QD array by colloidal dispersion
Up Conversion

Intermediate band solar cell

QE of a few % is useful
Er doped phosphors
– Shalav et al., PL (2005) 86, 013505
Triplet - triplet annihilation
- Baluschev et al., APL, 90 (2007), 181103

Bifacial solar cell
Phosphors in a transparent medium
Reflector

Solar cell
Up-converter
reflector

E_l
E_h
E_g
E_f
E_{relax}
J_l
J_h
J_{VC}
CB
VB
intermediate level
Potentialities and Viabilities

Requirements:
Higher efficiencies
Lower cost
Readily available & benign materials

Tandem cells
Already proven
Problems with reducing cost
Need breakthrough in cost structure

Thermal approaches - Hot Carrier cell
Potentially very high eff.
Long way from proof of concept

Up – Down Conversion
Can be applied to existing solar cells – big advantage
But early stages of proof of concept
Summary

• Relevance and growth of Photovoltaics
• Three PV Generations
• Main energy losses
• Third Generation approaches
• Si nanostructure tandem cells
  • Band gap eng.
  • Range of QD materials
  • Devices now up to 390mV $V_{OC}$
• Hot Carrier cells
  • Energy filter contacts
  • Phonon bottleneck
  • Nanostructures - QD based cell
• Up- and Down-conversion
• Third generation multi-energy level devices
  • tend to involve QD nanostructures
  • enable tailoring of material properties
Thank you for your attention

Research Staff:
  Martin Green, Richard Corkish, Gavin Conibeer, Dirk König, Eun-Chel Cho, Tom Puzzer, Yidan Huang, Shujuan Huang, Dengyuan Song, Santosh Shrestha, Ivan Perez-Wufl, Angus Gentle, Supriya Pillai

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