Solar Energy in MIB-Solar

Maurizio Acciarri, Simona Binetti, Alessandro Abbotto

MIBSOLAR and University of Milano-Bicocca, Department of Materials Science
MIB-SOLAR clean room

100 m² ISO 7 clean room

www.mibsolar.mater.unimib.it

fully equipped synthesis and characterization labs
Main facilities for the preparation of CIGS and DDSC cells and panels (sputtering system, nitrogen and argon filled glove box, laser scribing machine, titanium hotplates, screen printers, UV-ozone cleaners)

Main facilities for the full characterization of any solar devices (solar simulators up to 6 x 6 inches, I/V, EQE, light soaking chamber for cell ageing, stability studies, electrochemical impedance spectrometer).

Fully equipped laboratories for organic synthesis and characterization;

Fully equipped laboratories for optical, structural and electrochemical investigation (PL; PLE, ABS, Raman, XRD, EBIC, Hall set-up ..);
Research lines at MIBSOLAR

- Development of a new deposition procedure to growth Cu(InGa)Se2 thin film solar cells (M. Acciarri, S. Binetti, L. Miglio)
- Kesterite: a new material for thin film solar cells deposited by sputtering and chemical methods (S. Binetti, M. Acciarri)
- Nanocrystalline silicon solar cells (nc-Si:H) (S. Binetti, M. Acciarri, E. Bonera, M. Guzzi)
- Solar Grade Silicon (S. Binetti, M. Acciarri)
- Thin film Si QDs solar cells (M. Acciarri, S. Binetti)
- Light harvesting to increase the efficiency of silicon solar cells: (S. Binetti, M. Acciarri)
- Dye-Sensitized Solar Cells (DSC): Materials and Devices (A. Abbotto)
- Small-molecule and polymeric heterojunction solar cells: materials and devices (A. Abbotto, C. M. Mari, R. Ruffo)
- Solar cells of the third generation based thin and individual organic semiconductor crystal film(A. Sassella, A. Papagni, M. Moret, A. Borghesi)
- Panchromatic squaraines for hybrid and organic photovoltaic cells (G. A. Pagani L. Beverina)
- Structure and properties of photoactive materials for catalysis and organic-inorganic solar cells (G. Pacchioni, C. Di Valentin, L. Giordano).
- Computational Science conductivity in nanostructures: ab initio treatment of characteristic processes for the components of organic and hybrid photovoltaic cells(G.P. Brivio).

www.mibsolar.mater.unimib.it
The Centre owns its main skills, in the capture and conversion of solar energy from conventional crystalline silicon to new generation inorganic, organic and hybrid thin film devices.

- Silicon solar cells
- CIGS - CZTS thin film solar cells
- Triple junction solar cells (InGaP/GaAs/Ge)
- Light harvesting, spectrum modification
- Si Quantum dots solar cells
- Organic solar cells
- Dye sensitized solar cells
- Modeling and Theoretical activities
Inorganic Photovoltaic devices

M. Acciarri and S. Binetti group
Research lines: Silicon solar cells

Increase the ratio Efficiency /cost

- Use UMG Si
- Light harvesting
- 3th generation silicon based solar cells

Target 0.20 $/Wp – \eta = 40\%
Inorganic Photovoltaic materials and devices

- **c-Silicon solar cells**
  - Since 1990 involved in EU project on silicon solar cells
  - mc –Si: role of defects (dislocations, grain boundaries)
  - Metallurgical silicon: defect and compensation effect
  - Light harvesting, (EVA doped with Eu complexes)
  - multilayer quantum dots based material

  A.Le Donne et al. Optical Materials 33, 1012, (2011)

- **Inorganic thin-film technologies**
  - Cu(In,Ga)Se₂
  - CZTS

- **III-V based Tandem solar cells**
  - AllInGaP and AllInGaAs for 32% four junction devices for concentration application (CESI Spa)
  - GaAs grown on silicon: characterization (Pilegrowth s.r.l)

Research lines: Silicon solar cells

Advantages:
- lower cost
- lower energy payback time
- Lower carbon footprint

Metallic concentration can be reduced by:

Drawbacks:
- Low purity

But Internal gettering and metallic precipitates should be avoided

Contaminated with SiO₂
Clean, no EBIC C
Metallic precipitate (Ni, Fe)

UMG Silicon solar cells: effect on compensation

- Can lead to carrier lifetime improvements
- Reduction the light induced degradation effect (B-O complexes)


S. Binetti, G. Coletti, M. Acciarri IEEE PV 2014
Silicon sample for PV application grown under reduced melt convection

- Aim is to characterize solar silicon samples grown in microgravity conditions
- (ESA project A0-2009-1051 and Disk Project: a joint Russian-Europe Space Experiments)

**Advantages:**
- The melt flow has a laminar characteristic
- Close to diffuse regime
- Flat shape of the crystallization front

A. C. Wagner, A. Cröll, M. A. Gonik, H. Hillebrecht, S. Binetti

Light harvesting

Modify light spectra down converting photons with $E >> E_{\text{gap}}$ to photons with energy near the maximum quantum efficiency spectral region on the PV cell.

Modify light spectra down converting photons with $E >> E_{\text{gap}}$ to photons with energy near the maximum quantum efficiency spectral region on the PV cell.

$\Delta I_{\text{sc}} : +2.7\%$ (relative)

+0.6 % is sufficient to maintain unaffected the Wp price.

down-shifter dispersed in the encapsulant matrix
Si QDs solar cells

The Si QDs were formed by alternate deposition of SiO$_2$ and silicon-rich SiO$_x$ with magnetron co-sputtering, followed by high-temperature annealing.

Transport properties, and doping charge collection are crucial

*M. Morgano et al. Science of Advanced Materials 3, 388 (2011).*
Intermediate band photovoltaic cells

Evidence of two-photon absorption in strain-free quantum dot GaAs/AlGaAs solar cells

Nanostructured materials grown by Droplet epitaxy (DE), a molecular beam epitaxy variant, due to the absence of strain related defects, the high quality of the interfaces, the good confinement, and the capability to grow high density and large aspect ratio QDs, a perfectly suited system for the implementation of QD-IBSCs.

CIGS technology in UNIMIB

Thanks to the collaboration between the small enterprise Voltasolar S.r.L. and UNIMIB started in 2007, it has been developed an innovative industrial process for the production of the CIGS thin film on flexible substrate.

Project SolarDesign (contract no. FP7-NMP-2012-SME-6)
Projects Metadistretti 2008 e 2011 MIUR e Regione Lombardia
CIGS technology in UNIMIB

1. The metal precursors are sputtered on a cylindrical transferring body
2. Metals are then evaporated in Se ambient thanks to a local heating of the graphite elements of the transferring body
3. The process continue since the desiderate thickness is reached.

SUBSTRATI:
- 14 x 11 cm² soda lime glss 1 mm
- 20 x 10 cm² Cr stainless steel foil 125 um
- 20 x 10 cm² polyamide 25 um
- 14 x 11 cm² glass foil 125 um

Patent N° EP 13425019.0

Acciarri et al 2013. PCT European Appl., EP 13425019
CIGS characterizations

- Scanning electron microscope (SEM) with EDX (morphology and composition)
- XRF (composition)
- SIMS (University of Trento) (composition)
- Raman spectroscopy (phase identification)
- Photoluminescence (electrical properties)
- X-ray diffraction (phase identification)
- 4-probes method (resistivity)
- Profilometer (thickness)
- Tape-test (ASTM D 3359-02) (adhesion)
**S.I.M.S results**

- Double grading profile
- The “notch” region is less wide, closer to front contact.
- Decrease of CGI ratio close to 200 nm

5.5 keV Cs$^+$ sputter beam on 200x 200 µm$^2$

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* Dip di Fisica Università di Padova

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Cell finalization

Vacuum

- Evaporation
- Sputtering
- Sputtering metals + Evaporation Se
- Mo sputtering

Non vacuum

- 0.4 μm
- 300-350 nm
- 80- 100 nm
- 50-70 nm
- 2-2.5 μm
- 1 μm (Sol gel – SiOₓ)

CELL CHARACTERIZATIONS

- UV-visible Spectroscopy (CdS, ZnO, ITO optical properties)
- I-V curves (1.5 AM solar simulator) (solar cell properties)
- Scanning electron microscope (section)
- Spectral response (solar cell properties)
- Electron beam induced current (EBIC) maps (solar cell properties)
Best result on glass

η [%]: 14.5
Voc [mV]: 581.71
FF [%]: 72.0
Jsc [mA/cm^2]: 34.572
Area [cm^2]: 0.48
Irrad. mW/cm^2]: 100
# Best results on flexible substrates

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Eff (%)</th>
<th>Voc  (mV)</th>
<th>Jsc  (mA/cm²)</th>
<th>FF (%)</th>
<th>Area cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>130um glass</td>
<td>9.2</td>
<td>510</td>
<td>27</td>
<td>66</td>
<td>0.15</td>
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<tr>
<td>Stainless steal</td>
<td>13.1</td>
<td>569</td>
<td>34.1</td>
<td>70</td>
<td>0.15</td>
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<tr>
<td>Polyamide</td>
<td>11.7</td>
<td>512</td>
<td>35.6</td>
<td>64.34</td>
<td>0.15</td>
</tr>
</tbody>
</table>

130um glass

Polyamide 25 um

Stainless steal 125 um
From the laboratory to the pilot line

• In 2015, the first pilot line has been installed by Voltasolar in Austria (Sunplugged) and is under testing
• A Roll-to-roll deposition on wide flexible substrates (320 mm) (stainless steel or polyamide)
• Predicted productivity: 1.5-2 MW/y
Beyond CIGS solar cells

• Problems:
  – Toxicity (CdS as buffer layer)
  – Material shortage

• Solution:
  – Develop new buffer layers
  – Develop efficient thin-film (TF) photovoltaic (PV) absorbers based on earth-abundant elements!
  – $\text{Cu}_2\text{M(II)M(IV)S}_4$ chalcogenides using same deposition techniques of CIGS
  – Example: $\text{Cu}_2\text{ZnSnS}_4$
The deposition of the ZTO films was operated both from a ceramic target (75wt% ZnO – 25wt%. SnO₂) and from two metal targets (Zn and Sn) to form a metal bi-layer followed by an oxidation.
Buffer layer: Zn2SnO4 (c-ZTO)

- i-ZnO and AZO front contacts needs to be re-optimized for each new buffer layer.

### Table

<table>
<thead>
<tr>
<th>Size [cm²]</th>
<th>Power [W]</th>
<th>Jsc [mA/cm²]</th>
<th>Isc [mA]</th>
<th>Voc [mV]</th>
<th>FF [%]</th>
<th>Eta [%]</th>
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<tbody>
<tr>
<td>0.15</td>
<td>100</td>
<td>35.2</td>
<td>5.3</td>
<td>435.7</td>
<td>60.0</td>
<td>9.2</td>
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<tr>
<td>0.15</td>
<td>150</td>
<td>34.7</td>
<td>5.2</td>
<td>391.6</td>
<td>55.7</td>
<td>7.6</td>
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<tr>
<td>0.15</td>
<td>200</td>
<td>34.1</td>
<td>5.1</td>
<td>307.9</td>
<td>48.0</td>
<td>5.0</td>
</tr>
<tr>
<td>0.15</td>
<td>250</td>
<td>26.0</td>
<td>3.9</td>
<td>198.4</td>
<td>41.8</td>
<td>2.2</td>
</tr>
<tr>
<td>0.15</td>
<td>300</td>
<td>28.1</td>
<td>4.2</td>
<td>367.9</td>
<td>53.4</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Cu2ZnSnS4 (CZTS) by sputtering

1. Metal Precursors:
   - Sputtering RF from Cu, Zn, Sn (5N) target on 5x2 cm² Mo coated soda lime glasses (SLG)
   - Mo back contact deposited by DC magnetron sputtering (1 µm thick)

2. Sulphurization process:
   - 0.5 – 0.2 g of S in graphite crucible @ 250 °C in  
   - Ar flow = 30-40 cm³/min  
   - T= 550 °C

Working pressure

Sulphur
T = 250 °C

Ar inlet
Ar outlet

Tubular furnace

Resistance heater

Sample

450 °C

6 cm

30 cm

70 cm

Voc = 531 mV
Jsc = 16.6 mA cm⁻²
FF= 44.4 %
η = 3.95 %
CZTS by chemical method

CZTS absorber layer via drop casting

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH$_3$COO)$_2$ Cu · H$_2$O – 0.05 M</td>
<td>CH$_3$OH (90%)</td>
</tr>
<tr>
<td>(CH$_3$COO)$_2$ Zn · 2H$_2$O – 0.025 M</td>
<td>OHCH$_2$CH$_2$OH (10%)</td>
</tr>
<tr>
<td>SnCl$_2$ · 2H$_2$O – 0.025 M</td>
<td>+ PVA (0.50 ml)</td>
</tr>
<tr>
<td>H$_2$NCSNH$_2$ – 0.11 M</td>
<td></td>
</tr>
</tbody>
</table>

Annealing
1. SC(NH$_2$)$_2$ (l) $\xrightarrow{180-200 ^\circ C}$ NH$_2$CN (l) + H$_2$S (g)
2. @ 450 ℃ in S$_2$ Poliammide

Problems
- Spurius phases
- High rugosity
- $\eta < 1\%$

Project “Grande Rilevanza -Energy and Environment- “Nuovi materiali con basso impatto ambientale per la fabbricazione di celle solari a film sottile” – Protocollo Esecutivo ITALIA-EGITTO

Thermoelectric Heat Recovery in Single Junction Solar Cells

3rd Gen PV devices (DSSC, OPV, PSC)

3rd Gen Solar fuels
PHOTOSENSITIZERS:
I. Polypyridine and polyquinoline complexes (Ru$^{II}$, Ir$^{III}$)
II. Cyclometalated complexes
III. Porphyrins
IV. Metal-free organic dyes
V. p-Type dyes
VI. Perovskites (PSC)

ELECTROLYTES:
1. Iodine-free electrolytes
2. Quasi solid-state electrolytes

TiO$_2$:
1. Hierarchical nanostructures
2. Dye-uptaking

DEVICE
1. Fabrication and Characterization
2. Cells and Modules
3. Hybrid technologies (Si-CIGS-DSSC-perovskites)
MULTIBRANCHED DYES: enhanced photocurrent

In collaboration with

DSSC record EQE with Ru(II) dyes

MLCT
\[ \varepsilon = 16000 \text{ M}^{-1} \text{ cm}^{-1} \]
(14000 M\(^{-1}\) cm\(^{-1}\) in benchmark complex)

EXTERNAL QUANTUM EFFICIENCY
electrons out
photons in

(benchmark dye: max 87%)

Branched organic dyes: evolution

Multi-Branched Multi-Anchoraging Metal-Free Dyes for Dye-Sensitized Solar Cells

Norberto Manfredi,*[a] Bianca Cecconi,[a] and Alessandro Abbotto*,[a]

Keywords: Solar cells / Dyes/Pigments / Sensitizers / Energy conversion / Photochemistry

Iodine-free electrolyte

Redox potentials

From 0.35 V (iodine) to 0.92 V (Fc) + 0.6 V available for photovoltage!
ssDSSC and PSC

Novel air-stable Hole transporting material

molecular

polymeric
Building-integration PV (BIPV)

Integrated Photovoltaic Glass Tiles for Innovative Architectural Applications
Luminescent solar concentrators

Prof. F. Meinardi and S. Brovelli group.

‘Stokes-shift-engineered’ CdSe/CdS quantum dots with giant shells (giant quantum dots) were used to realize luminescent solar concentrators without reabsorption losses for device dimensions up to tens of centimetres.

Study of these luminescent solar concentrators yields optical efficiencies >10% and an effective concentration factor of 4.4. These results demonstrate the significant promise of Stokes-shift-engineered quantum dots for large-area luminescent solar concentrators.
ss-Hybrid technologies

Monolithic solid state devices

Target
- moderate scenario $\eta=17\%$
- optimistic scenario $\eta=21\%$
Hybrid technologies

<table>
<thead>
<tr>
<th>Type</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC</td>
<td>6.0</td>
</tr>
<tr>
<td>CIGS</td>
<td>7.1</td>
</tr>
<tr>
<td><strong>DSC/CIGS</strong></td>
<td><strong>8.4</strong></td>
</tr>
</tbody>
</table>

![Diagram of solar cell structure](image1)

![Graphs showing PCE and current density](image2)
“water will be the coal of the future”

Jules Verne

*The Mysterious Island*

1874

TOWARD A LOW-CARBON SOCIETY

HORIZON 2020
Natural photosynthesis

\[ \text{H}_2\text{O} \xrightarrow{hv} \text{"H}_2" + \frac{1}{2} \text{O}_2 \]

CO₂

carbohydrates

Artificial photosynthesis

\[ \text{H}_2\text{O} \xrightarrow{hv} \text{H}_2 + \frac{1}{2} \text{O}_2 \]

The chemical challenge:
High transformation efficiency from electron to hydrogen

Thanks to Prof. S. Abbotto
Clean sources of Water Splitting

2-step
- electrical power
- PV-driven electrolysis
- too expensive!

1-step
- integrated device (PEC, photocatalysis)
- cheaper but low currents!

\[ \text{H}_2 + \text{O}_2 \]
Towards artificial photosynthesis

Water electrolysis through DSC

Dye-Sensitized Solar Cells

Water Splitting with Solar Energy

Thanks to Prof. S. Abbotto
Energy store

H₂
Energy store

H₂ → CH₄ → CO₂
Energy store
Upgrading technologies

• Upgrading of biogas or landfill gas to biomethane is defined as removal of carbon dioxide from the biogas.
• This will result in an increased energy density since the concentration of methane is increased to up to 95%.
• Several technologies for biogas upgrading are commercially available and others are at the pilot or demonstration level.
Smart upgrading

Principal phases of our process:

• absorption CO₂ in the **solvent** in the cold column
• Solvent heating for the CO₂ release (temperature below 75°C)
• CO₂ collection and solvent regeneration in the hot stripping
• Solvent cooling
• Solvent reintroduction in the cold absorption column

Solvent based on Ionic liquid
• no toxic
• low cost
2016: Industrial production plant under pianification

Lab scale 1 m³/h
2012

pilot scale 100 m³/h
2014

Pre-Industrial scale
2015

Presso CEM Ambiente Cavenago (MB)
Biomethane and CO2: energy storage and “sequestration”

- Biogas produced through anaerobic digestion is often used as a source of combined heat and power (CHP).

- **For use as a transport fuel** as well as **for natural gas grid injection**, biogas must be cleaned and upgraded to typically greater than 97% methane content (then known as biomethane).

- Another advantage is that the biomethane can be used to generate electricity in combined cycle gas turbines that can produce electricity from methane with efficiency above 60%.

- CO₂ can be easily accumulated ... and CO₂ is ready to go as a fuel and chemical feedstock (Electrolysis, Artificial leaves, catalytic water splitting, CO₂ reduction, Biotechnology)
Biogas an example of Circular Economy

- **Substrates**
  - Biogas production
  - Purification/upgrading (H2O, S, CO2, .. removal)
  - Biomethane

- **Energy Storage**
  - H2
  - Methane
  - Energy Storage

- **Electricity**

- **Heat**

- **Gas to grid**

- **Fuel for cars**

- **Green Chemistry**

- **Renewable energy**

- **Social impact**

Economical aspects
Photovoltaics could become an important source of energy, but this won't happen by chance.

Thanks

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