Non radiative energy transfer mediated high efficiency radial p-n junction hybrid solar cells using nanocrystalline Si quantum dots and Si nanowires

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Background

1. **Purcell** (1946): Vacuum photon field induced emission from an excited molecule can be manipulated by changing field around it.
   - Unverified till 1960

2. **Forster**: Direct dipole-dipole interaction between molecules can transfer energy from one molecule to another
   - Verified by many researchers in bio-imaging and other fields

3. **Drexhage** (1960): Radiative decay rate of an emitting molecule near metal surface
   - Semiconductor cavity quantum electrodynamics
   - Photophysics of molecules as a function of the distance

4. **Dexter** (1985): Proposed quantum mechanical theory of the energy transfer from an excited molecule to underlying direct or indirect band gap semiconductor

   Very recently, nonradiative energy transfer (NRET) has been proposed for hybrid nanostructures that combine absorbing components (e.g., quantum dots) with high-mobility semiconducting channels.
Metal-catalyzed electroless etching (MCEE)

Si substrate

→ Treatment with Piranha solution

→ Cleaned Si substrate

→ Si NW arrays with Ag dendrites

Steps:
- EtOH
- Aceton
- HF
- AgNO₃
- HNO₃

Treatment with Piranha solution:
- H₂SO₄
- H₂O₂

Net reaction:
Si + 6HF → H₂SiF₆ + 4H + 4e⁻

Scale: 2 µm
Growth of radial junction: CVD deposition

n-type Si nanowires

p-n radial junction
p-n Core shell structure vs. n-SiNWs embeded in p-Si matrix structure

<table>
<thead>
<tr>
<th>sample</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (Ω/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Si NW arrays embedded in p-Si</td>
<td>0.46</td>
<td>24.4</td>
<td>0.6</td>
<td>7</td>
<td>2.4</td>
</tr>
<tr>
<td>Core-shell structure</td>
<td>0.41</td>
<td>23</td>
<td>0.5</td>
<td>4.71</td>
<td>4.6</td>
</tr>
</tbody>
</table>

- Al ~ 100 nm
- Ag ~ 100 nm

Synthesis of colloidal nc-Si QDs and hybrid cells

Hydrogen silsesquioxane (HSQ) → Rotary Evaporation → Gel → Vacuum Dry → White solid → 1100°C H₂/Ar → Bulk nc-Si/SiO₂

Mesityline + 1-octadecene + Hydride terminated nc-Si → Decantation → 145°C → Transparent yellow solution → Washing

1:1:1 Ethanol, HF, H₂O + Fine powder → Grinding → Fine powder

Centrifuge → Toluene, methanol → Spin cast

Quantum yield ~ 30%

Morphological and spectroscopic characterisations of nc-Si QDs

- Average diameter ~ 3.7 nm
- Lattice interplanar spacing of 0.31 nm

Enhancement in conversion efficiency in presence of nc-Si QDs

![Current-Voltage Characteristic](image1)

- Current (mA/cm^2)
- Voltage (V)
- With nc-Si QD
- Without nc-Si QD

![Efficiency vs. Wavelength](image2)

- EQE
- Wavelength (nm)
- With nc-Si QDs
- Without nc-Si QDs

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<th>$R_{sh}$ (Ω/cm^2)</th>
</tr>
</thead>
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<tr>
<td>nc-Si QD modified hybrid cell</td>
<td>0.47</td>
<td><strong>38.70</strong></td>
<td>0.71</td>
<td><strong>12.9</strong></td>
<td>0.34</td>
<td>7059.2</td>
</tr>
<tr>
<td>Without QD modified cell</td>
<td>0.47</td>
<td><strong>32.67</strong></td>
<td>0.71</td>
<td><strong>10.9</strong></td>
<td>0.38</td>
<td>4882.7</td>
</tr>
</tbody>
</table>

X-ray photoelectron spectroscopic observations

Band alignment at the interface of p-Si layer and nc-Si QDs.

Energy transfer from nc-Si QDs to Si layer

- $\tau_{\text{RET}} \sim (20.9 \ \mu s)^{-1}$, $\tau_{\text{NRET}} \sim (12.9 \ \mu s)^{-1}$
- Non radiative energy transfer rate is $\sim 1.6$ times faster than radiative energy transfer rate

Advantages of ET mediated solar cell architecture

1. Reduction of spectrum loss by greater solar light absorption cross section due to the absorption of the UV region of the solar spectrum by using nc-Si QDs.

2. Resonant excitation transfer from nc-Si QDs to the adjacent Si layer accompanied by the spontaneous creation of electrons and holes.

3. Efficient electron and hole separation in p-n junctions and transport in oppositely doped high mobility Si channels.

4. Very low series resistance due to low contact resistance as a result of continuous front contact fabrication.

- This architecture free from the bottleneck of exciton separation and transport in excitonic solar cells.
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